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MASTER

Reliability of Materials for Solar Energy

December 18-20, 1978

Workshop Proceedings

Volume II

Part II

Workshop Proceedings

Sponsored by

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Solar Energy Research Institute

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Golden, Colorado 80401

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MASTER

RELIABILITY OF MATERIALS FOR SOLAR ENERGY

WORKSHOP PROCEEDINGS

VOLUME II

PART 2

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DECEMBER 18-20, 1978

DENVER, COLORADO

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Volume II

Part 2

Presentations and Papers

from the workshop on

RELIABILITY OF MATERIALS

FOR

SOLAR ENERGY SYSTEMS

December 18 - 20, 1978

Sponsored by:

The Solar Energy Research Institute

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LOW-COST SILICON ARRAYS

Viewgraphs Presented

by

Dale Burger

Jet Propulsion Laboratory

Pasadena, California

LOW-COST SOLAR ARRAY PROJECT

SILICON PV CELL PROCESSES VS. TIME

PROCESS CATEGORY	1975	1978	TIME 1982*	1986*
DAMAGE ETCH	HF	HF/NaOH	NaOH	PLASMA
DIFFUSION	POCL ₃	POCL ₃	POCL ₃ /ION	POCL ₃ /ION
BACK SURFACE	PVD	PLATING/SS	SILK SCREEN	SILK SCREEN
GRID MASK	PR SILK SCREEN	PR SILK SCREEN	SILK SCREEN	?
GRID	PVD	PLATING	SILK SCREEN	SILK SCREEN/ ION
A-R	PVD	SPIN	SPRAY/ROLLER	ROLLER
INTERCONNECT	SOLDER	SOLDER	US, SOLDER	?

* PROJECTED

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LOW-COST SOLAR ARRAY PROJECT

SILICON PV CELL MATERIALS VS TIME

MATERIAL CATEGORY	1975	1978	TIME 1982*	1986*
SILICON GRADE	SEMICONDUCTOR	SEMICONDUCTOR	SOLAR CELL (PILOT)	SOLAR CELL
WAFER TYPE	CZ	CZ	RIBBON (PILOT)	RIBBON
FRONT CONTACT	TI-PD-AG AU-NI AG INK	AU-NI-SOLDER AG INK	AG INK PD-NI-CU	?
BACK CONTACT	"	"	AL PD-NI-CU CU	?
INTERCONNECT	TINNED CU	TINNED CU	AL	?

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LOW-COST SOLAR ARRAY PROJECT

SILICON PV CELL MATERIAL HANDLING VS. TIME

FACTORY AREA	TIME			
	1975	1978	1982*	1986*
INGOT	MANUAL CZ	MANUAL CZ	AUTOMATED CZ	?
WAFERING	SAW	MBS MWS ID SAW	MBS MWS AUTO. ID SAW	(AUTO. RIBBON)
CLEANING	MANUAL WASH CASSETTE WASH	PLASMA PATCH CASSETTE WASH	AUTO. PLASMA	AUTO. PLASMA
DIFFUSION	MANUAL LOAD	MANUAL LOAD AUTO LOAD	AUTO. ION AUTO. DIFF	(BELT FURNACE) (AUTO. ION)
METALLIZATION & AP	MANUAL TRAY	CASSETTE MANUAL	CASSETTE LINE	BELT LINE
INTERCONNECT	HAND	HAND	AUTO. STRING	AUTO ASSEMBLE

* PROJECTED

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FIELD TESTING OF ELECTRON CIRCUITS

by

William H. Abbott

Battelle Columbus

Columbus, Ohio

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LOW-COST ENCAPSULATION MATERIALS FOR
TERRESTRIAL PHOTOVOLTAIC MODULES

Viewgraphs Presented

by

Edward F. Cuddihy
Jet Propulsion Laboratory
Pasadena, California

LOW-COST SOLAR ARRAY PROJECT PROJECT COST GOALS BY 1986

- TOTAL MODULE COST

50 ¢/WATT (\$5.00/ft², 1975 DOLLARS)

- ENCAPSULATION MATERIALS COST

2.5 ¢ TO 5.0 ¢/WATT (25 ¢ TO 50 ¢ PER ft²)

ENCAPSULATION REQUIREMENTS

- OUTDOOR LIFETIME 20 YEARS
- OPTICAL TRANSMISSION OF MODULE COVER > 90%
- TRANSMISSION DECREASE IN 20 YEARS < 20%
- PROCESSING AND FABRICATION AUTOMATED
- STRUCTURAL PERFORMANCE NO FAILURES
(INCLUDING HANDLING AND WEATHERING)

FLAT MODULE DESIGN CLASSIFICATIONS

1) SUBSTRATE BONDED

2) SUPERSTRATE BONDED

3) LAMINATED
A) RIGID

i)

B) FLEXIBLE

ii)

MODULE DESIGN CONCEPTS

DESIGN OPTIONS

- 1) SUBSTRATE BONDED
- 2) SUPERSTRATE BONDED
- 3) LAMINATED
 - A) RIGID, SELF-SUPPORTING
 - B) FLEXIBLE
 - i) SUBSTRATE SUPPORTED
 - ii) SUPERSTRATE SUPPORTED

CONSTRUCTION ELEMENTS

- 1) TRANSPARENT OUTER COVERS
 - A) SOIL RESISTANT
 - B) UV ABSORBING
- 2) TRANSPARENT POTTANTS
- 3) ADHESIVES
- 4) SUBSTRATE
- 5) TRANSPARENT SUPERSTRATE
- 6) SUPERSTRATE BACKSIDE POTTANTS AND/OR BACK COVERS

KNOWN WEATHERABLE AND TRANSPARENT MATERIALS

MATERIALS

- GLASS
- ACRYLICS
- SILICONES
- FLUOROCARBONS
AND HALOCARBONS

EXAMPLE

- SODA-LIME WINDOW GLASS
- PLEXIGLAS, LUCITE
- SYLGARD 184, RTV 615
- TEDLAR, FEP,
KEL-F RESINS

ECONOMICS OF MODULE FABRICATION WITH KNOWN WEATHERABLE AND TRANSPARENT MATERIALS

<u>MATERIAL</u>	<u>AS TRANSPARENT STRUCTURAL SUPERSTRATES</u>	<u>AS POTTANTS ADHESIVES OUTER COVERS</u>
GLASS	\$0.29 TO \$1.00/ft ²	—
ACRYLICS	\$1.77/ft ²	≤ \$.01/ft ² - mil
SILICONES	\$45.00/ft ²	\$.02-.05/ft ² - mil
FLUOROCARBONS HALOCARBONS	\$12-\$23/ft ²	> \$.05/ft ² - mil

MATERIAL SURVEYS

- SURVEY ALL MATERIALS FUNCTIONAL (OPTICAL, STRUCTURAL, ETC.) FOR EACH CONSTRUCTION ELEMENT
- ESTABLISH COST-COMPARISON BASIS FOR EACH ELEMENT
- IDENTIFY LOWEST-COSTING MATERIALS IN EACH ELEMENT CLASS, DETERMINE LOWEST COST FOR EACH ELEMENT, AND INDICATE LOWEST ACCUMULATIVE MATERIAL COST FOR ENCAPSULATION SYSTEMS
- IDENTIFY DEFICIENCIES (WEATHERABILITY, PROCESSABILITY, ETC.) OF LOWEST-COST MATERIALS, ASSESS CAPABILITY AND/OR FUTURE DEVELOPMENTAL ACTIVITIES NEEDED TO OVERCOME DEFICIENCIES
- SCALE-UP AS NECESSARY TO HIGHER-COSTING MATERIALS, SEEKING OPTIMIZATION OF COST, PERFORMANCE, ASSEMBLY, AND LIFE

SUBSTRATES/SUPERSTRATES

COST COMPARISON BASIS

EDGE-REINFORCED PANEL, 45 INCHES LONG BY 15 INCHES WIDE,
WITH CALCULATION OF MINIMUM THICKNESS AND THEREFORE
COST PER ft^2 REQUIRED FOR A CENTER-POINT DEFLECTION OF
NO GREATER THAN 1/4 INCH UNDER A UNIFORM WIND LOADING
OF 50 lbs/ft^2 ($\approx 100 \text{ mph WIND}$)

DEFLECTION RESISTANCE*, $Et^3 = 9,280 \text{ lbs-in}$

E = MODULUS

t = MINIMUM THICKNESS

* REFERENCE

R. J. ROARK, FORMULAS FOR STRESS AND STRAIN, 4th EDITION, p. 225,
MC GRAW-HILL (1965)

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SUBSTRATES/SUPERSTRATES

MATERIAL CLASSES BEING SURVEYED

EXAMPLES

INORGANICS

CEMENT BOARDS, TILES, BRICKS, ETC.

PAPER PRODUCTS

KRAFT PAPER HONEYCOMBS, PRESSED PAPERBOARD
PANELS, ETC.

WOOD PRODUCTS

PLYWOOD, HARDBOARD, PARTICLE BOARDS, ETC

GLASS

SODA LIME GLASS, BOROSILICATES, ETC.

METALS

STEEL, ALUMINUM, ETC.

PLASTICS

GLASS-REINFORCED POLYESTER, PHENOLICS, ETC.

SUBSTRATES/SUPERSTRATES

MATERIALS AND COSTS

- INORGANICS, SURVEYS IN PROGRESS

- PAPER PRODUCTS

- PAN-L BOARD, MEAD PAPERBOARD PRODUCTS, INC. 24¢/ft²
WEATHERPROOFED AND WATERPROOFED, 17 YEARS OUTDOOR
EXPOSURE IN WISCONSIN,
- KRAFT PAPER HONEYCOMB, HEXCEL CORPORATION, 9¢/ft²
- HOMASOTE, INC., PAPER PANEL 13.6¢/ft²

SUBSTRATES/SUPERSTRATES

MATERIALS AND COSTS

(CCB = COST-COMPARISON BASIS)

● WOOD PRODUCTS

COST PER ft²

	<u>CCB</u>	<u>COMMERCIAL</u>
● PLYWOOD, CLASS C, PLUGGED	14.3¢	1/4 inch, 17¢
● MASONITE EXTERIOR HARDBOARD (SUPER-DCRLUX®)	13.3¢	1/8 inch, 10¢ 1/4 inch, 14¢
● PARTICLE BOARDS	13.8¢	1/4 inch, 13¢
i) WAFER BOARDS		
ii) STRAND BOARDS		
iii) FLAKE BOARDS

SUBSTRATES/SUPERSTRATES

MATERIALS AND COSTS

- GLASS

SODA LIME GLASS
OTHERS

\$0.29/ft²
>> \$0.29/ft²

- METALS

MILD STEEL
ALUMINUM
STAINLESS STEEL

\$0.42/ft²
\$1.15/ft²
\$3.16/ft²

- PLASTICS

STRUCTURAL POLYPROPYLENE
POLY VINYL CHLORIDE EXT. PANEL
OTHERS

\$0.49/ft²
\$0.59/ft²
\$0.72 TO \$4.08/ft²

- TRANSPARENT
PLASTICS

PLEXIGLAS, LUCITE (ACRYLICS)
LEXAN (POLYCARBONATE)

\$1.77/ft²
\$3.41/ft²

SUBSTRATES/SUPERSTRATES

TENTATIVE CONCLUSIONS

- WOOD PRODUCTS AND PAPER PRODUCTS LOWEST-COSTING STRUCTURAL SUBSTRATE MATERIALS
- SUPERSTRATE DESIGN EMPLOYING TRANSPARENT PLASTICS IS ECONOMICALLY UNATTRACTIVE, OPTION WITH GLASS STILL VIABLE

SUBSTRATES/SUPERSTRATES

DEVELOPMENTAL NEEDS

- HIGH STRENGTH-TO-WEIGHT RATIO PANEL DESIGNS FOR LOWER-COST UTILIZATION OF STRUCTURAL MATERIALS

EXAMPLE: CENTER REINFORCEMENT OF SUBSTRATE PANEL LOWERS THICKNESS REQUIREMENT AND PANEL COST BY A FACTOR OF 2.47, PAN-L BOARD COST BECOMES 10¢/ft

- WATERPROOFING AND WEATHERPROOFING OF WOOD PRODUCTS

TRANSPARENT POLYMERIC POTANTS

- COST COMPARISON BASIS: COST PER ft^2 PER mil
- MODES OF OUTDOOR WEATHERING DEGRADATION
 - 1) THERMAL OXIDATION
 - 2) HYDROLYSIS (WATER REACTIONS)
 - 3) UV REACTIONS
 - a) JV PHOTOLYSIS
 - b) UV PHOTO-OXIDATION
 - c) UV PHOTO-HYDROLYSIS
- SURVEY FOR TRANSPARENT MATERIALS WHICH ARE INHERENTLY WEATHERABLE, AND THOSE WHICH ARE SUSCEPTIBLE TO DEGRADATION FROM UV REACTIONS ONLY (ASSUMES THE USE OF A UV-SCREENING OUTER COVER)

TRANSPARENT POLYMERIC POTTANTS

CANDIDATE MATERIALS

<u>WEATHERABLE WITH UV PROTECTION</u>	<u>MATERIAL COST PER POUND</u>	<u>MODULE COST CENTS/ft²-mil</u>	<u>MAXIMUM THICKNESS AT \$.06/ft², mils</u>
ETHYLENE VINYL ACETATE	\$.50	0.17	35
ETHYLENE PROPYLENE TERPOLYMER	\$.65	0.28	21
POLY VINYL CHLORIDE PLASTISOL	\$.60	0.33	18

WEATHERABLE

ACRYLICS	\$1.50	1	6
SILICONE GELS	\$3.75	2	3
SILICONE ELASTOMERS	\$9.00	5	≈ 1
FLUOROCARBONS AND HALOCARBONS	\$6.75 TO > \$20	> 5	≤ 1

TRANSPARENT POLYMERIC POTANTS

ODDS AND ENDS

- LOWEST COSTING TRANSPARENT POLYMER IS 23¢/lb, CORRESPONDS TO A MAXIMUM THICKNESS OF 50 mils at 6¢/ft²
- ISOLATED FROM UV, ETHYLENE VINYL ACETATE HAS ENDURED 15 YEARS OUTDOOR EXPOSURE TO DATE
- POLYVINYL CHLORIDE POSITIONED BEHIND A TRANSPARENT, BUT UV-ABSORBING FILM (TEDLAR UT), HAS ENDURED 4 YEARS OUTDOOR EXPOSURE TO DATE

ETHYLENE VINYL ACETATE (EVA)

COMMERCIAL SUPPLIERS

DUPONT "ELVAX"

U. S. I. CHEMICAL CO. "VYNATHANE"

STATUS

- ENCAPSULATION-GRADE EVA FORMULATED (SPRINGBORN)
- EXPERIMENTAL FILMS EXTRUDED (20 MILS)
- 10 TO 15 EVA ENCAPSULATED MODULES FABRICATED
 - VACUUM-BAG PROCESS
 - 11 X 16 INCH
- EVA/GLASS PRIMERS IDENTIFIED
 - SS 4179 GENERAL ELECTRIC
 - HYDROLYZED Z-6030 DOW CORNING

SILICONES

MATERIALS (DOW CORNING)

XI-2577	5.2 ϕ /ft ² /mil
DL840/B48N	1.2 ϕ /ft ² /mil

STATUS

- EXPERIMENTAL SPRAYABLE FORMULATIONS DEVELOPED
- 11 X 16 INCH MODULES FABRICATED
- CELL/GLASS ADHESIVE/PRIMER SYSTEM IDENTIFIED
 - Q3-606C GLASS PRIMER
 - XI-2561 ADHESIVE

TRANSPARENT OUTER COVERS

COST COMPARISON BASIS: COST PER ft^2 PER mil

REQUIREMENTS: TRANSPARENT

INHERENTLY WEATHERABLE

SOIL RESISTANT (MODULUS $>20,000$ psi)

UV ABSORBING

MATERIAL CANDIDATES:	GLASS	$\approx 0.3¢$
	ACRYLICS	$\approx 1¢$
	SILICONES	$\approx 5¢$
	FLUOROCARBONS AND HALOCARBONS	$\geq 5¢$

TRANSPARENT OUTER COVERS

UV-ABSORBING FILMS

- COMMERCIAL

TEDLAR UT	4.82¢/ft ² /mil	DuPONT	(FLUOROCARBON)
KORAD 201-R	≈2¢/ft ² /mil	EX-CELLO	(EXPERIMENTAL ACRYLIC)

- DEVELOPING

ACRYLIC	≈1¢/ft ² /mil	SPRINGBORN LABORATORIES
SILICONE	COST, ? -	DOW CORNING

SOILING OF EXTERIOR SURFACES

ENVIRONMENT

- ATMOSPHERIC ORGANICS
- RELATIVE HUMIDITY / DEW
- PARTICULATES (SOLUBLE, NON-SOLUBLE)

MATERIAL

- SURFACE HARDNESS
- WATER RELATED PROPERTIES
 - i) PERMEATION
 - ii) SOLUBILITY
 - iii) SWELL
- STICKY MATERIAL PRODUCTS
 - i) AT MANUFACTURE
 - ii) FROM WEATHERING

OUTDOOR SOILING EXPERIENCE OF PHOTOVOLTAIC MODULES FABRICATED WITH DIFFERENT EXTERIOR SURFACES

POWER RECOVERY AFTER CLEANING

	SOFT SILICONE ELASTOMERS		SILICONE	
	RTV615	SYLG. 184	HARD COAT	GLASS
DSET 161 days	+ 9	+ 9	+ 4	+ 1
Caribbean (1 yr.)	+ 9	+ 9	0	+ 2
MIT	+ 13 (5 mo.)	+ 14	+ 10 (5 mo.)	+ 6 (5 mo.)
NYU	+ 23 (6)	29 (5)	22 - 26	+ 11
	+ 33 (12)	38 (12)		
Columbia U.	21 (6)	22 (6)	-	+ 12 (6)
	29 (12)	33 (12)		

↑
DECREASING
OIL, RH
ENVIRONMENT

↓
INCREASING
SURFACE
HARDNESS

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PERMEATION PROPERTIES OF POLYMERS

F & G VALUES FOR PERMEATION AT 30°C

(THE PRODUCTION FG GIVES THE PERMEABILITY CONSTANT $\times 10^{10}$ IN CC(STP) - mm/cm²/sec/cm Hg)

<u>POLYMER</u>	<u>F VALUES</u>	<u>POLYMER</u>	<u>F VALUES</u>
SARAN	0.0094	"VULCAPRENE"	4.9
TEDLAR	0.033	CELLULOSE ACETATE (15% DEP)	5.0
"MYLAR"	0.050	"HYCAR" OR 25	6.04
"PLIOFILM" NO	0.080	"PLIOFILM" P4	6.2
NYLON 6	0.10	"PERBUNAN"	10.6
"KEL-F"	1.3	NEOPRENE	11.6
"PLIOFILM" FM	1.4	POLYETHYLENE (0.92 g/ml)	20.0
"HYCAR" OR 15	2.35	BUNA-S	63.5
POLYVINYL BUTYRAL	2.5	POLYBUTADINE	64.5
CELLULOSE ACETATE P-912	2.8	NATURAL RUBBER	80.0
BUTYL RUBBER	3.12	ETHYL CELLULOSE (PLASTICIZED)	84.0
METHYL RUBBER	4.8	SILICONE RUBBER	106.0
<u>GAS</u>	<u>G VALUES</u>	<u>GAS</u>	<u>G VALUES</u>
NITROGEN	1.0	HYDROGEN SULFIDE	21.9
OXYGEN	1.9 TO 3.8	CARBON DIOXIDE	24.2
		WATER VAPOR	40 TO 35,000

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SOILING RESISTANCE AND MAINTENANCE

DESIGN FACTORS

- HARD SURFACES
- OLEOPHOBIC AND LOW HYGROSCOPIC
- MATERIAL FREE OF STICKY COMPONENTS

OPERATIONAL MAINTENANCE

- RESURFACING (SAND BLASTING DAMAGE)
- WASHING MODULES WHILE WET WITH DEW
- DETERGENT/SOLVENT SOLUTIONS

DESIRED GOAL

SURFACES READILY CLEANABLE BY NATURAL MEANS
(WIND, RAIN, DEW, ETC.)

ADHESIVES

COST COMPARISON BASIS: COST PER ft^2 PER 5 mil GLUE LINE

- FLUOROCARBONS $> 9-10¢$
- SILICONES $9-10¢$
- ACRYLICS $4¢$
- EPOXIES $\leq 4¢$
- OTHERS $< 4¢$

PARTIAL REQUIREMENTS: 100% ADHESIVE MATERIAL, NO VOLATILE SOLVENT OR WATER CARRIER, NO GAS PRODUCTS RELEASED DURING SET OR DURING OUTDOOR SERVICE

ADHESIVES

WATER-TIGHT INTERFACES

- ADHESIVES AND PRIMERS WHICH ARE CHEMICALLY REACTIVE WITH INTERFACING SURFACES PROMOTE WATER-TIGHT INTERFACES

INDUSTRIAL EXAMPLES

- i) GLASS FIBER REINFORCED PLASTICS
- ii) SILICONE ENCAPSULATED TELEPHONE CIRCUITRY

- ION-PLATED COATINGS (e.g., ALUMINUM OXIDE)

LAMINATED DESIGN SUMMARY

LAMINATED DESIGN

- RIGID LAMINATED DESIGN SEEMS IMPROBABLE - NEED TO USE HIGH-MODULUS TRANSPARENT PLASTIC (COST, EXPANSION COEFFICIENT MISMATCH, ETC.)
- FLEXIBLE LAMINATED DESIGN SEEMS PROBABLE EMPLOYING LOW-COST SUBSTRATE, AND LOWEST-COST TRANSPARENT POLYMERS FOR NECESSARY LAMINATING THICKNESS

ADVANTAGE: APPLICABLE TO EXISTING STRUCTURAL SURFACES, ROOFS, GROUND, ETC.

COST SUMMARY

● SUBSTRATE DESIGN

	<u>COST/ft²</u>
1 mil UV-ABSORBING OUTER COVER	\$.01
TRANSPARENT POTTANT	.06
ADHESIVES	.04
WOOD OR PAPER PRODUCT SUBSTRATE	<u>.14</u>
TOTAL	\$.25

● SUPERSTRATE DESIGN

TRANSPARENT PLASTICS	> \$1.77
GLASS	
BACKSIDE POTTANT	\$.06
ADHESIVES	.04
WINDOW GLASS	<u>.29</u>
TOTAL	\$.39

DESIGN TRADE-OFF CONSIDERATIONS

GLASS SUPERSTRATE DESIGN VS. SUBSTRATE DESIGN

- RUNS COOLER
- RESISTS HAIL
- RESISTS DIRT

MATERIAL-INFLUENCED DESIGN CONSIDERATIONS

- COOLEST METAL SUBSTRATE
- CLEAREST GLASS SUPERSTRATE
- CHEAPEST WOOD/PAPER SUBSTRATE

THE FUTURE

- ACCELERATED/ABBREVIATED LIFE PREDICTION METHODOLOGY
- SOILING RESISTANCE AND MAINTENANCE
- DEVELOPMENT OF AUTOMATED PROCESSING TECHNIQUES
 - APPROPRIATELY FORMULATED MATERIALS
- OPTIMAL MODULE DESIGN
 - COST
 - STRUCTURAL
 - OPTICAL
 - LIFE
 - PROTECTION OF CELLS, INTERCONNECTS, WIRES, ETC.
- CONTINUE MATERIALS IDENTIFICATION AND DEVELOPMENT
 - UV SCREENS, POTTANTS, PRIMERS
 - SUBSTRATES/SUPERSTRATES

LSA ENCAPSULATION TASK OBJECTIVES

- MEASURE AND PREDICT RATES OF PHOTODEGRADATION
- DESIGN ACCELERATED TESTS FOR MATERIALS AND SUBSYSTEMS
- MAKE RECOMMENDATIONS FOR MATERIAL MODIFICATIONS TO MEET LSA ENCAPSULANT LIFETIME AND RELIABILITY GOALS

LSA ENCAPSULATION TASK APPROACH

- MECHANISM OF PHOTODEGRADATION

- MEASURE AND INTEGRATE SOLAR ULTRAVIOLET

MATERIALS UNDER INVESTIGATION

- LEXAN
- PMMA
- PMMA CONTAINING UV SCREENING MATERIALS
- EVA
- SILICONES (POLYDIMETHYLSILOXANE)

LSA ENCAPSULATION TASK

MECHANISM OF PHOTODEGRADATION

- STEADY STATE RATE MEASUREMENTS

FT-IR
UV/VISIBLE

SPECTROSCOPY

GPC

MOLECULAR
WEIGHT

SEA

SURFACE
ENERGY
ANALYSIS

- FLASH PHOTOLYSIS

- TRANSIENT ABSORPTION OF REACTIVE EXCITED STATES

- LIFETIMES
 - CHARACTERIZATION OF SPECIES

- TRANSIENT EMISSION

- IDENTIFICATION OF AROMATIC IMPURITIES
 - EXCITED STATE LIFETIMES

LSA ENCAPSULATION TASK

ACCELERATED TEST DESIGN CRITERIA

MATERIAL

PROPERTIES WHICH
INTERACT WITH STRESS
e.g. ABSORPTIVITY,
MOBILITY (GLASS
TRANSITION TEMP) etc

CHANGE IN MOLECULAR PROPERTIES

- RATES
- MECHANISMS
AS FUNCTION OF
 - UV (WAVELENGTH,
INTENSITY)
 - TEMPERATURE
 - O_2 , H_2O
CONCENTRATION

STRUCTURE OF SUBSYSTEM

- COMPOSITE
ABSORPTIVITY
- COMPOSITE
DIFFUSION RATES

ACCELERATED UV TEST CHAMBER FOR ONE CELL MODULES OF SUBSTRATE DESIGN

SPECTRORADIOMETRIC ANALYSIS OF IRRADIANCE AT SAMPLE PLANE (R. ESTAY), AND 1.0 AM SOLAR IRRADIANCE (NBS)

pdf

FILM ACTINOMETER

- QUANTUM YIELD = 0.50 ± 0.03 , INDEPENDENT OF WAVELENGTH (250 - 400 nm)
- ACTIVATION ENERGY < 0.5 k Cal/mole
- RANGE OF RESPONSE ≤ 410 nm
- CAN BE INCORPORATED IN POLYMERIC FILMS
- READ BY IR SPECTROSCOPY
- USABLE RANGE OF CONVERSION: 51%

THE STABILITY AND RELIABILITY OF CdS/Cu₂S SOLAR CELLS

by

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University of Delaware

Newark, Delaware

THE STABILITY AND RELIABILITY OF CdS/Cu₂S SOLAR CELLS

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I. Introduction

A photovoltaic effect in CdS was first reported in 1954 by Reynolds¹ for a junction made by electroplating a film of copper onto an indium doped CdS crystal and then heating the crystal to 350°C. Later work established that the junction was between CdS and Cu₂S.² A great number of research and development efforts have followed since this initial discovery with the majority focused on thin film polycrystalline cells for either space or terrestrial use. An exhaustive review of the work up to 1973 has been published by Stanley.³

Many different cell designs have been developed and a wide variety of techniques used to deposit the constituents and to make electrical contacts. However, since the National Aeronautical and Space Administration sponsored work at the Clevite Corporation,⁴ the majority of the effort has been devoted to improving the vapor deposited thin film polycrystalline cell first developed in that program. The cell is constructed by vapor depositing a 20 to 40 μm thick CdS layer on a thin metal substrate or a metallized plastic film. A short etch in hydrochloric acid produces a heavily textured light trapping surface which is then reacted in a CuCl solution to produce a layer of Cu₂S 0.1 to 1.0 μm thick. The top electrical contact is then generally made with a metal grid using a variety of techniques such as vapor deposition, electroplating or pressure contacting.

Many features of the structure and operation of the cell were unknown or poorly understood during the first twenty years or so of development. Major difficulties were encountered in the reliable production of high efficiency cells and many cells were found to be unstable and rapidly decayed below their initial efficiency. Lack of knowledge on the structure and operation of the cell, as first produced, resulted inevitably in an almost bewildering range of mechanisms being proposed to explain the observed decay in performance with time.

Figure 1 shows a schematic cross section of a typical vapor deposited thin film CdS/Cu₂S cell. This figure shows a front wall cell (light incident through the Cu₂S); backwall cells utilize a transparent conducting layer for the substrate e.g. SnO₅ or CdSn₂O₄⁶ on glass and the top contact can then be replaced by an opaque conductor. The basic operation of the CdS/Cu₂S heterojunction has now been well established and is reviewed in detail by Rothwarf and Barnett.⁷ The ideal efficiency for the CdS/Cu₂S junction without any losses is $\sim 16\%$ and the practical achievable efficiency is estimated to be 11%. Cells of a conversion efficiency above 9.0% have been reported by the Institute of Energy Conversion of the University of Delaware.⁸ Figure 2 shows the band diagram that is believed to apply to

high efficiency CdS/Cu₂S cells.

Almost all the photon absorption and minority carrier generation takes place in the Cu₂S layer. The generation efficiency is determined by photon losses and the minority carrier loss mechanisms such as surface and bulk recombination in the Cu₂S and interface recombination at the CdS/Cu₂S junction. Measured short circuit currents have shown that the Cu₂S surface is generally well passivated and that bulk recombination rates are strongly dependent on the Cu₂S stoichiometry. The effectiveness of interface recombination depends on the balance between the drift field in the CdS, F_2 and the interface recombination rate S_I . Rothwarf⁹ has shown that the fraction of electrons successfully crossing the interface is given by

$$\mu F_2 / (S_I + \mu F_2)$$

where μ is the electron mobility in the CdS. Measurement of dark and light capacitance has shown that the collection field is much enhanced in the light as a consequence of hole trapping in the junction region.

The open circuit voltage achievable is limited to about 0.57 V by the electron affinity mismatch between Cu₂S and CdS indicated in Figure 2. In addition, V_{oc} can be further reduced by junction area effects and high field regions.⁷ Good cells show diode factors of 1 and hence the fill factor can in principal be as high as 80%; inhomogeneous fields and series and shunt resistances reduce the achievable fill factors to the 70-75% range.

2. CdS/Cu₂S Life Testing

The early life testing of thin film CdS/Cu₂S cells was aimed at establishing performance data relevant to space missions. Measurements of electrical performance were made at various temperatures under a range of illuminations. In addition, severe thermal cycling tests were conducted to simulate space mission conditions. Definitive analysis of the life performance data was hampered in many cases by the poor reproducibility of cell production and by the still developing understanding of the cell structure and operation. The large spread in initial cell properties was reflected in a wide variation of apparent cell stability.

Work under National Aeronautical and Space Administration sponsorship at the Clevite Corporation has been summarized in a number of publications.^{4,10,11} A major result of the NASA studies was the identification of copper nodule growth as a primary degradation mechanism. Cells exposed to light under open circuit conditions were found to degrade rapidly and microscopic examination of cell cross-sections identified copper filament and nodule growth as the cause of the decay. Tests on cells loaded to various voltages indicated that a threshold voltage between 0.35 and 0.4 V⁹ was necessary to cause copper nodule growth for the type of cell under test.

The Boeing Aerospace Corporation conducted a number of stability studies of Clevite cells for NASA¹² The cells were either maintained at 55°C under constant illumination or were cycled for 60 minutes illumination, 30 minutes darkness resulting in a temperature cycle from -100°C to 60°C. Cells were

illuminated by a Xenon simulator while maintained in a dynamic vacuum of $\sim 10^{-6}$ torr; the cells were loaded to close to the maximum power point. No attempt was made to analyze the cause of failure or degradation. It was concluded that the most significant parameter controlling the rate of degradation was the date of manufacture of the cell suggesting that structural and compositional factors were dominant. No significant differences were detected between continuous and intermittent illumination. Testing covered the range from 2,500 to 15,000 hours and resulted in efficiency losses from as little as 3% to as much as 29%. One or two cells even showed a 1 or 2% increase in efficiency. It should be noted that the initial power conversion efficiencies were generally in the range of 2 to 3%.

Researchers at a number of laboratories in France have made major contributions to the understanding and control of cell degradation. In 1973¹³ the full importance of the stoichiometry of the Cu_2S layer was recognized and the loss of stoichiometry by oxidation was established. Life testing showed that the degradation rate was slower at better vacuums. Doping of the CdS with an unspecified dopant was also reported to result in improved stability even under open circuit conditions. Extended test results on the 1973 cells were recently reported.¹⁴ Table 1 shows the results of exposing

Table 1

Life Testing of CdS/ Cu_2S Cells¹⁴

Exposure to AMO at 60°C under Vacuum for 7000 Hours
Initial CdS/ Cu_2S Efficiency $\sim 6.7\%$

<u>Cell</u>	<u>$\frac{\Delta J_{sc}}{J_{sc}}$</u>	<u>$\frac{\Delta FF}{FF}$</u>	<u>$\frac{\Delta \eta}{\eta}$</u>
CdS/ Cu_2S - Kapton	-8.3%	+2.0%	-7.5%
CdS/ Cu_2S - Aclar	-37.3%	+0.3%	-39.3%
Silicon - Aclar	-34.0%	-1.5%	-37.2%

Exposure to 95% Relative Humidity at 40°C for 5000 Hours[†]

<u>Cell</u>	<u>$\frac{\Delta J_{sc}}{J_{sc}}$</u>
CdS/ Cu_2S - Aclar	90%
CdS/ Cu_2S - Glass	1%

cells to AMO at 60°C under a dynamic vacuum. Much of the efficiency degradation noted for the Aclar covered cells can be attributed to loss of transparency of the Aclar. Kapton is a more satisfactory cover but is not sufficiently impervious to prevent loss in performance. Cells hermetically sealed behind glass do however seem to be essentially stable under the conditions tested. After 5000 hours at 40°C and 95% relative humidity, the short circuit current has declined by only 1%, a change that is probably

[†] Illumination not specified.

within the experimental error. The 7000 hour test was stated to be equivalent to six years terrestrial deployment.

Corroboration of the French results is provided by the tests of Clevite cells performed by Westinghouse.¹⁵ Groups of cells were sealed behind glass and maintained at 40, 60, 80 and 100°C. The cells were loaded to the maximum power point and illuminated at AM1 for a 12 hours on 12 hours off cycle. The decline in the average efficiency of groups of four cells after 18 months exposure was 3.4, 0, 3.1 and 32% at 40, 60, 80 and 100°C, respectively. In all cases, the fill factors declined (3.6, 4.3, 12.1, 29%) but at 60 and 80°C this was offset by substantial improvements in short circuit current.

Various accelerated and roof top tests have also been conducted at I.E.C.¹⁶ on Clevite cells and also on cells produced at I.E.C. under NSF/RANN sponsorship. Cells were maintained in a variety of flowing gasses at various temperatures and exposed to simulated AM1 illumination either continually or for one hour on one hour off cycles. All cells maintained in dry air degraded more than 20% in seven months. Considerable variability was observed in the cells maintained under Argon or Nitrogen with a few cells showing negligible degradation after seven months.

The life testing briefly reviewed above has shown conclusively that cells will generally degrade rapidly if exposed to air. In the following section, evidence will be reviewed which shows that such degradation is at least in large part due to oxidation of the Cu_2S layer which lowers the stoichiometry of the Cu_2S layer. Cells well protected from oxidation by either dynamic vacuums or by encapsulation behind glass have shown minimal degradation rates implying that the basic heterojunction structure is capable of long term stability. Probably the longest "test" on record was reported by D. C. Reynolds¹⁷ for an epoxy encapsulated array of 13 back wall single crystal cells made by the Harshaw Company in 1957. No special precautions were taken to store the array and testing 17 years later showed no detectable degradation from the original performance of 8.2 V open circuit voltage and 9.5 mA short circuit current.

Until stability measurements under deployment conditions can be interpreted in terms of specific degradation mechanisms, projections of usable lifetimes are at best subject to considerable uncertainty. This is even more true of efforts to use accelerated life testing to forecast deployment lifetimes. Such testing will be discussed further in Section 4.

3. Analysis of Degradation Mechanisms

Oxidation of Cu_2S

The loss of cell performance caused by oxidation of the Cu_2S is probably the most definitively established degradation mechanism and is responsible for many of the early reports of cell instability. The reaction is, however, reversible and can be expressed as follows

Under oxidizing conditions, the heat of formation of the Cu_2O will drive the reaction to the right but under strongly reducing conditions, the reaction is reversed and the initial stoichiometry can be restored. Figure 3 shows that little oxidation is needed to substantially change the stoichiometry of the Cu_2S layers typical of the high efficiency cells now being made at I.E.C. A discussion of the influence of Cu_2S stoichiometry on short circuit current and Cu_2S sheet resistivity is presented elsewhere.⁹ It is sufficient for present purposes to point out that virtually the highest achievable stoichiometry and the concomitant highest sheet resistivity is necessary to achieve the maximum short circuit current. Figure 4 reveals how rapidly the sheet resistance of unprotected Cu_2S decays in air. The figure also shows partial recovery of the resistivity with a brief reducing heat treatment. A more extensive treatment will fully restore the resistivity to the initial value. Figure 5 shows how the actual I-V behavior of a cell is degraded by oxidation and can be restored by a reducing treatment.

Diffusion of Cu into CdS

It is well established that copper diffuses from the Cu_2S into the CdS and results in a compensated region. Measurement of the dark capacitance as a function of time and temperature have been used to estimate the width of the compensated region¹⁸ and to determine the diffusion coefficient of Cu in CdS. Excessive copper diffusion has been suggested as a cause of degradation and estimates of usable deployment life have been made assuming standard thermal activation relationships.

A number of mechanisms have been proposed to explain loss of performance because of copper diffusion. It has been suggested that the series resistance contribution of the compensated region will become sufficient to lower the fill factor.¹⁹ Other suggestions are that the loss of copper from the Cu_2S or the reduced field in the junction region will give lowered short circuit currents.

The gradual widening of the compensated layer is well documented but recent work at I.E.C. has shown that this is not associated with a loss in short circuit current. Table 2 shows that while the dark capacitance declines rapidly with heat treatment, the capacitance under AM1 illumination is changing much more slowly. Trapping of light generated holes near the $\text{Cu}_2\text{S}/\text{CdS}$ junction is believed responsible for the high capacitance in the light but the important point to make here is that the field at the junction and hence the current collection efficiency is relatively insensitive to protracted high temperature exposure. Recently made high efficiency cells (> 8.5%) are routinely exposed to 170°C for over 50 hours during manufacture. The contribution of the CdS resistivity to the total cell series resistance has been found to be insignificant even after these protracted heat treatments. Fill factors of over 70% are routinely achieved after heat treatments exceeding 100 hours at 170°C.

Table 2

Influence of Heat Treatment on
Dark and Light Capacitance and Short Circuit Current

Cell #	State	Capacitance nF/cm ²		J_{sc} mA/cm ²
		Dark	Light	
668 A1-1	Initial	12.0	98	15.5
668 B1-1	Initial	18.4	99	16.4
673 A1-1	Initial	11.1	66	16.0
673 B1-1	Initial	12.4	73	18.0
668 A1-1	12 hours, 170°C	8.16	98	15.8
668 B1-1	12 hours, 170°C	9.93	96	17.1
673 A1-1	12 hours, 170°C	5.82	66	16.9
673 B1-1	12 hours, 170°C	6.53	73	17.8
668 A1-1	20 hours, 190°C	2.10	89.1	16.4
668 B1-1	20 hours, 190°C	2.94	88.0	18.0
673 A1-1	20 hours, 190°C	1.35	60.2	18.1
673 B1-1	20 hours, 190°C	1.43	69.5	18.4

Electrolytic Decomposition of Cu₂S

Electrolytic decomposition of Cu₂S is a well documented fact.²⁰ If a sufficient potential difference is maintained across a chalcocite sample, copper will plate out at the cathode and reduced stoichiometry sulfide will form at the anode. The necessary threshold voltage at the copper deficient boundary of chalcocite, Cu_{1.995}S²¹ can be computed from thermodynamic data to be 0.265 V. Assuming that the activity of copper varies linearly with composition over the chalcocite phase, the threshold voltage will fall in a linear manner to zero at the Cu₂S boundary where chalcocite is in equilibrium with copper. Actual measurements show a slight overvoltage above the thermodynamic values²⁰ possibly due to the kinetics of copper nucleation. In an actual cell the major potential drop is across the CdS and only as the Cu₂S approaches ideal stoichiometry can any potential be supported by the Cu₂S. Present knowledge of the relative conductivities of the Cu₂S and CdS layers suggests that the threshold voltage will never be reached. Even if the Cu₂S layer was initially ideally stoichiometric and hence approached an insulator, the increase in threshold voltage as copper plates out at the CdS/Cu₂S junction ensures that the process is self limiting and decomposition would terminate when only a fraction of a monolayer of copper had formed.

The situation is completely different in a structurally imperfect cell where deep cracks or pores in the CdS become coated with Cu₂S. Under these conditions, the Cu₂S layer can be subjected to substantial electric fields resulting in sufficient copper deposition to provide shorting paths to the base electrode. Such copper growths have been directly observed¹⁰ and the existence of deep channels and defects established.²² In summary, the evidence available suggests that cells constructed on defect free CdS will be immune to electrolytic decomposition of the Cu₂S.

There is an alternative origin of a potential gradient in the Cu_2S which does not seem to have received attention in the literature. With a wide grid spacing, the inhomogeneous current density in the Cu_2S will create a potential gradient from the grid line to the mid-line position. If sufficient potential is developed, this will result in the establishment of a lateral stoichiometry gradient. The impact of this on cell performance and stability remains to be established.

Structural Instabilities

A multi component composite structure such as the $\text{CdS}/\text{Cu}_2\text{S}$ cell can fail or degrade in a variety of structural ways unrelated to the actual heterojunction. The extreme temperature cycling to which cells were subjected during the N.A.S.A. program was shown to cause delamination at the substrate- CdS interface.¹⁰ Many possibly polymeric encapsulants are known to lose transparency and structural integrity when exposed to ultra violet radiation. In retrospect, it is clear that many cell failures were caused by loss of electrical contact between the Cu_2S and pressure bonded gridding systems. Reviewing the current state of knowledge, it is not apparent that there are any structural failure modes which cannot be successfully designed against. There will, however, have to be substantial development efforts to produce both reliable and economically acceptable techniques for cell gridding and encapsulation.

Summary

It is concluded that the research and testing conducted to date has identified the major cell degradation mechanisms none of which preclude the production of cells with usable lifetimes of 10 to 20 years. The quantitative data needed to determine the rate of degradation for terrestrial deployment is generally lacking, due in part to changes in cell design and improvements in initial cell performance. To obtain such data in the short term will require the successful development of accelerated testing procedures which is the subject of the next section.

4. Accelerated Life Testing

In many technologies, it has proved possible to develop highly reliable accelerated testing procedures, e.g. short term creep testing to forecast service life. To do so requires detailed knowledge of the degradation mechanism being accelerated. In the case of thin film solar cells and $\text{CdS}/\text{Cu}_2\text{S}$ specifically, such knowledge is not available. Most of the accelerated life tests to date have utilized elevated temperatures and enhanced illumination (either intensity or duration) to hasten degradation. If indeed there is degradation due to thermally activated processes, then high temperatures will increase its rate. However, before meaningful data interpretation and computation of equivalent lifetimes at deployment temperatures is possible, such activated mechanisms must be identified and thermal coefficients or activation energies determined. Similarly, problems exist in equating five hours of continuous illumination to 24 hours of deployment. Unless it can be shown that degradation occurs solely under illumination or that there are recovery mechanisms active in the dark, such equivalences

are without foundation. The almost universal weakness of all published accelerated life test data is that observed degradation has not been matched to specific changes in the cell. Meaningful accelerated testing will not be possible until specific degradation mechanisms are identified and acceleration procedures matched to the mechanisms.

5. Research Needs

In order to project cell lifetimes under deployment conditions, it is essential to determine the degradation mechanisms taking place and their effect on cell performance. Attention should clearly be focused on those mechanisms which are intrinsic to the junction and which exist in high efficiency cells. There is little merit in laboriously cataloguing the decline of cells which initially had efficiencies below usable levels. If oxidation of the Cu_2S can occur, it is now well documented that this will cause major loss of output. Accordingly, to determine other life limiting effects, the cells tested must be made resistant to this mode of degradation. The following are seen as the major research needs which when satisfied will allow life projections of the $\text{CdS/Cu}_2\text{S}$ cell to be made with confidence.

1. A quantitative description of the interaction of oxygen with the Cu_2S layer and the associated structural and electronic changes. Associated with this study should be the development of either ideal hermetic sealing or the measurement of diffusion rates through non-ideal encapsulations.
2. The identification of those inter-diffusion mechanisms which reduce cell performance and the measurement of their time-temperature characteristics.
3. The identification of structurally related degradation modes such as delamination and loss of grid contact and their relation to deployment conditions.
4. Identification of the detailed relation between copper nodule formation and CdS structure and properties. Confirmation that nodules do not form during exposure equivalent to 15-20 years deployment.

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Figure 1. Cross section of a typical CdS/Cu₂S cell.

Figure 2. Band diagram for a CdS/Cu₂S cell. The conduction band discontinuity is 0.2-0.3 eV. A population of hole trapping centers lying deep in the band gap in the compensated CdS is indicated. These exist to the extent of the compensated region, W_0 . W_{2i} is the width of the space charge region in the dark.

Figure 3. The influence of oxidation on the stoichiometry and hole density of initially stoichiometric chalcocite.

Figure 4. The reduction of Cu_2S sheet resistance on exposure to air and recovery by a reducing heat treatment.

Figure 5. Loss of short circuit current on exposure to air and recovery by reducing heat treatment. The initial and final sunlight efficiency is 8.6%, the degraded state corresponds to 6.3%. Above I-V curves taken under W I simulation.

GOALS AND NEEDS

Viewgraphs Presented

by

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THE LARGER PICTURE:

- DOE EXPECTS PHOTOVOLTAICS TO PROVIDE 50 GIGAWATTS BY THE YEAR 2,000
- CELL ARRAY CONVERSION EFFICIENCY REQUIREMENT IS 10% OR GREATER
- THE ARRAYS MUST LAST 20 YEARS WITH AN ALLOWABLE DEGRADATION FROM INITIAL PERFORMANCE OF 5%
- CELL COSTS SHOULD DECREASE TO \$2/PEAK WATT BY 1982, 50¢/PEAK WATT BY 1986, AND 10-30¢/PEAK WATT BY 1990-2000 FOR SOLAR PHOTOVOLTAIC POWER TO BE COMPETITIVE (1975 DOLLARS)

MEETING THESE SIMULTANEOUS NEEDS REQUIRES THAT FORMIDABLE TECHNICAL PROBLEMS MUST BE FACED AND OVERCOME

ASSETS - APPARENT & OTHERWISE

1. SIMILAR PROBLEMS IN NON-PHOTOVOLTAIC DEVICES

(A) GENERAL

1. SOLAR CELL PROBLEMS $\geq$ INDUSTRY & DOD PROBLEMS FOR IC'S, PWR XSISTORS & DIODES. IN PARTICULAR, G_{AS} CONCENTRATOR CELLS ARE SUBJECT TO MOST OF THE SAME FAILURE MODES FOUND FOR μ WAVE IC'S & DISCRETES, GUNN & LASER DIODES.
2. BTL'S CONCERN WITH CORROSION IN IC'S LEAD TO THEIR DEVELOPMENT OF ADVANCED TECHNIQUES (TEST PATTERNS) TO MAGNIFY & REVEAL EARLY OCCURRENCE.

(B) HUMIDITY

1. LITERALLY A "LIFE-OR-DEATH" CONCERN, WITH LEGAL IMPLICATIONS, TO PACEMAKER MFRS. NBS WORKSHOP HELD. TECHNIQUES & TEST STRUCTURES CONSIDERED.
2. FIRST CAUSE OF XSISTOR FAILURE. HOW IS THIS MINIMIZED IN TODAY'S PLASTIC-ENCAPSULANT IC'S?

ASSETS - APPARENT & OTHERWISE CONT.'D

2. DON'T REINVENT THE WHEEL!

- (A) A "NEW" ADVANCE IN SOLAR CELLS: HARRICK'S & GUNN'S MID-FIFTIES WORK REEMERGES 20 YRS LATER.
- (B) "PURPLE PLAGUE" REVISITED. (DoD ACCELERATED TESTING YIELDED A BOGUS FAILURE MODE IN IC'S BUT MAY MASK CORROSION INCLINATION).
- (C) TUNNEL CONTACTS FOR "STACKED" SOLAR CELLS VS. DEGRADATION OBSERVED IN G_{AS} TUNNEL DIODES 15 YRS. AGO.

WE SHOULD BE GENERALISTS AS WELL AS SPECIALISTS, AND SEARCH RELATED FIELDS TO UNDERSTAND RELIABILITY, AND DEGRADATION MODES, FOR OTHER DEVICES AS WELL AS SOLAR CELLS.

3. ENHANCE MANPOWER & FACILITY RESOURCES. IF FROM INDUSTRY, ESTABLISH & MAINTAIN CONTACTS WITH:

(A) UNIVERSITIES

(B) GOVERNMENT LABORATORIES. CONSIDER:

1. THEY MAY HAVE WELL-FUNDED PROGRAMS IN FAILURE-ANALYSIS (DoD).
2. THEY MAY HAVE UNIQUE/EXPENSIVE EQUIPMENT
3. YOU ARE A TAXPAYER.
4. "RELEVANCE" IS ONE OF TODAY'S KEY WORDS.

TRANSPORT IN THERMALLY GROWN SILICA ON SILICON

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TRANSPORT IN THERMALLY GROWN SILICA ON SILICON

J. Bruce Wagner, Jr.
18 December 1978

OXIDATION OF SILICON

TWO GENERAL OBJECTIVES:

1. DIELECTRIC FOR ELECTRONICS
2. PROTECTIVE COATING FOR HIGH TEMPERATURE MATERIALS

OXIDATION STUDIES CAN BE DIVIDED INTO ROUGHLY THREE REGIMES:

1. VERY HIGH TEMPERATURES
E.G. AT OR ABOVE MELTING POINT OF SILICON. VOLATILE SiO(g) FORMS AND RATE IS DETERMINED BY GAS TRANSPORT ACROSS BOUNDARY LAYER. (REFERENCES: W. KAISER AND J. BRESLIN, J. APPLIED PHYS. 29, 1293 (1958); C. WAGNER, IBID 29 1295 (1958).)
2. HIGH TEMPERATURE
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$$n_O = n_O^0 + RT \ln p_{O_2}^{1/2}$$

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$$x^2 + Ax = B(t + \tau)$$

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$$B = 2 D_{\text{EFF}} C^*/N.$$

$$\tau = (x_i^2 + Ax_i)/B$$

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N = NUMBER OF OXIDANT MOLECULES INCORPORATED INTO A UNIT VOLUME OF OXIDE LAYER.

FOR $t, x \rightarrow \infty$

$$x^2 \approx Bt$$

$$\chi^2 = k_T T$$

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$$\frac{k_T}{\chi} = k_R = \frac{1}{F^2} \int_{\mu'_O}^{\mu''_O} \left[\frac{1}{|Z_\theta|} \frac{\sigma_{ion} \sigma_{elec}}{\sigma} \right] d\mu_O$$

WHERE k_R = RATIONAL RATE CONSTANT IN EQ/CM²-SEC

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μ'_O, μ''_O = CHEMICAL POTENTIAL OF OXYGEN AT THE Si-SiO₂ AND THE SiO₂-O₂ INTERFACE, RESPECTIVELY.

AND

$$\mu_O = \mu_O^0 + RT \ln p_{O_2}^{1/2}$$

Z_O = VALENCE OF OXYGEN IN SiO₂

σ = TOTAL ELECTRICAL CONDUCTIVITY

$$\sigma = \sigma_{ion} + \sigma_{elec}$$

WHERE

$$\sigma_{ion} = \text{IONIC CONDUCTIVITY}$$

$$\sigma_{elec} = \text{ELECTRONIC CONDUCTIVITY}$$

Si	SiO ₂	Si
----	------------------	----

Si	SiO ₂	Ge _{1-x} Si _x
----	------------------	-----------------------------------

Si	SiO ₂	PO ₂
----	------------------	-----------------

$$E = \frac{RT}{F} \int_{p'_{O_2}}^{p''_{O_2}} \left[\frac{t_{ion}}{n} \right] d \ln p_{O_2}$$

F = Faraday's

p'_{O_2} , p''_{O_2} = oxygen pressures at Si-SiO₂ and SiO₂-gas interfaces respectively.

t_{ion} = transport number for ion

n = number of equivalent transported per 1 gm mole O₂; hence if n_{76}^- diffuses, $n = 4$

THREE TYPES OF DATA ARE NEEDED:

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2. ISOTHERMAL OXIDATION KINETICS AS A FUNCTION OF OXYGEN PARTIAL PRESSURE.

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SOME PHYSICAL PROPERTIES

	Si	SiO ₂
MOL. WT., GM/MOLE	28.06	60.06
MELTING PT., °C	1410	1610
DENSITY, GM/CM ³ (20°)	2.34	2.5
CRYSTAL STRUCTURE	DIAMOND CUBIC	AMORPHOUS OR GLASSY & SEVERAL CRYSTALLINE FORMS
IR ADS. (S-O)	---	1090 CM ⁻¹
DIELECTRIC BREAKDOWN (25°)	---	5 TO 1 x 10 ⁶ V/CM.

Po₂ (Si-SiO₂, 900°C)

~ 10⁻²⁹ ATM

ΔG° (SiO₂, 298°K)

- 139 KCAL/MOL

TRANSPORT IN THERMALLY GROWN SILICA ON SILICON

Viewgraphs Presented

by

J. Bruce Wagner, Jr.

Arizona State University

Tempe, Arizona

OXIDATION OF SILICON

TWO GENERAL OBJECTIVES:

1. DIELECTRIC FOR ELECTRONICS
2. PROTECTIVE COATING FOR HIGH TEMPERATURE MATERIALS

OXIDATION STUDIES CAN BE DIVIDED INTO ROUGHLY THREE REGIMES:

1. VERY HIGH TEMPERATURES
E.G. AT OR ABOVE MELTING POINT OF SILICON. VOLATILE SiO(g) FORMS AND RATE IS DETERMINED BY GAS TRANSPORT ACROSS BOUNDARY LAYER. REFERENCES: W. KAISER AND J. BRESLIN, J. APPLIED PHYS. 29, 1293 (1958); C. WAGNER, IBID 29 1295 (1958).
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Si	SiO ₂	Si
----	------------------	----

Si	SiO ₂	Ge _{1-x} Si _x
----	------------------	-----------------------------------

Si	SiO ₂	Por
----	------------------	-----

$$\mu_O' \quad \mu_O''$$

$$\mu_O = \mu_O' + RT \ln p_{O_2}^{1/2}$$

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Porous Pt

Porous

κ_z

Accelerating Field - electrode

No Field

Retarding Field + electrode

850°C

t (hr.)

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SUMMARY

1. OXYGEN IS MOBILE SPECIES
2. WHETHER OXYGEN IS MONATOMIC OR DIATOMIC IS NOT DEFINITE
3. CHARGE(S) ON OXYGEN NOT DEFINITE
4. ADDITIONAL RESEARCH NEEDED:
 - (A) ISOTHERMAL, ISOBARIC KINETICS FROM $X=0$ TO $X > 5000\text{\AA}$ IN DRY OXYGEN
 - (B) ISOTHERMAL KINETICS AS FUNCTION P_{O_2}
 - (C) TEM, SEM STUDIES ON SiO_2 FILMS
 - (D) GALVANIC CELL STUDIES TO OBTAIN IONIC TRANSPORT NUMBER
 - (E) CONDUCTIVITY STUDIES ON SILICA GROWN ON SILICON

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SOME PHYSICAL PROPERTIES

	Si	SiO ₂
	MOL. WT., GM/MOLE MELTING PT., °C DENSITY, GM/CM ³ (20°) CRYSTAL STRUCTURE IR ADS. (S-O) DIELECTRIC BREAKDOWN (25°)	28.06 1410 2.34 DIAMOND CUBIC --- --- 60.06 1610 2.5 AMORPHOUS OR GLASSY & SEVERAL CRYSTALLINE FORMS 1090 CM ⁻¹ 5 to 1 x 10 ⁶ V/CM

Po₂ (Si-SiO₂, 900°C)
 ΔG° (SiO₂, 298°K)

 ~ 10⁻²⁹ ATM
 - 139 KCAL/MOL

LINEAR CONCENTRATING SOLAR COLLECTORS--
CURRENT TECHNOLOGY AND APPLICATION

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ABSTRACT

This report surveys linear concentrating collector technology. Included are fundamentals of the technology; descriptions of collectors with particular emphasis on the types tested at the DOE/Sandia Midtemperature Solar Systems Test Facility (MSSTF); performance test results; problems identified through operating experience; cost projections; and a discussion of applications of linear concentrating and midtemperature solar collectors.

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Introduction

The objective of the Dispersed Power Systems Program within the Department of Energy's (DOE) Division of Solar Technology is to foster research and development for large-scale commercial implementation of dispersed solar thermal power systems. This comprises irrigation pumping, solar total energy systems, small (less than 10 MW) solar electric power plants, and high-temperature process heat applications. The word "dispersed" distinguishes between applications in which the solar plant is located at the point of use, and centralized (or utility) applications in which a large solar electric power plant serves a grid-connected, widespread market.

Sandia Laboratories manages Solar Total Energy and Irrigation, while the Jet Propulsion Laboratory of Pasadena, California, manages Small Power Systems Applications. Sandia also has two other closely related projects in support of Dispersed Power Systems. These are the Application Technology Development (ATD) project and the Midtemperature Solar Systems Test Facility (MSSTF).

The objective of ATD is the development of components and subsystems and the generation of technical data. This includes materials and process investigations, development of operation and maintenance (O&M) expertise, and characterization and measurement techniques development.

The primary objective of the MSSTF project is to support the application projects of the Dispersed Power Systems Program by:

1. providing a facility sufficiently versatile to be used as an engineering evaluation center or test bed for solar energy components and subsystems,
2. providing realistic system design and integration experience,
3. generating performance and cost data on components and subsystems,
4. accumulating O&M experience,
5. developing expertise in the private sector, including "hands on" experience, and
6. distributing mechanical, cost, and maintenance

information gained from the testing to potential developers and users of solar energy.

The ATD and MSSTF projects together support the application projects of the Dispersed Power Systems Program. Components are developed in ATD based on projected requirements of DOE or commercial application projects--the real installations in the real world. The MSSTF is utilized as a test bed to evaluate these components and to identify, through operating experience, areas requiring additional research and development.

A major activity within both the ATD and MSSTF projects is to develop and evaluate concentrating solar collectors that are efficient at elevated temperatures. Line-focusing collectors constitute the vast majority of concentrators now in service and the type with which Sandia has the most experience. The rest of this report surveys linear concentrating collectors, their performance capabilities, cost projections, and applications.

Linear Concentrating Collector Fundamentals

The fundamental operating concept of all line-focusing solar collectors is the same--solar radiation incident on a concentrating device is concentrated on a receiver through which a heat-transfer fluid flows. The concentrator may be either a reflector or a lens. The receiver is usually round tubing or pipe, but some designs employ non-round cross sections. Although the heat-transfer fluid may be either liquid or gas, no designs using gas are presently in field service.

Except for industrial process heat, all dispersed power system applications involve thermodynamic processes and are therefore subject to Carnot's laws, suggesting that high temperatures are advantageous. These applications will be discussed in more detail later in the report. While collectors designed for high-temperature operation can be considered for lower temperature applications,

the reverse may not be true. A geometric concentration factor of 25 or above is typical of collectors designed for high-temperature operation. Many excellent, cost-effective, concentrating collectors are marketed in the 10 range, but this discussion is limited to collectors designed for operation at temperatures above 235°C. Most of these are, in fact, designed for 300°C. Above this temperature two materials limitations, heat-transfer fluids and selective absorber coatings, presently constrain the technology.

All high-concentration line-focusing collectors track the sun throughout the day to maintain the sun's image on the receiver. Most reflective concentrators track in one axis only because the sun's position is critical relative to the concentrator's cross section only and need not be normal to the longitudinal axis. Collectors may be oriented along an east-west longitudinal axis and track the sun's elevation angle, or along a north-south axis and track the sun in azimuth. Lens concentrators differ from reflectors in that they must track the sun in two axes so that the incident solar radiation is normal to the focal plane of the lens. Nonnormality in the longitudinal axis reduces focal length and correspondingly reduces energy density at the receiver tube.

Throughout the following descriptions of collectors, reference is made to the reflecting surface. Three families of materials--polished metals, metallized films, and silvered glass--are generally employed.

Polished metals typified by Alcoa's Alzak and Kingston Industries' King Lux are moderately expensive (approximately \$20.00/m²) but are very durable, stable over long exposure times, are easily procured in sheet form, and can readily be bent and fastened to a curved substrate. The specular reflectance characteristics of these materials are their major drawback. Although these materials have a total hemispherical reflectance of about 0.85, their specular reflectance to a 10 mrad receiving aperture is only about 0.70.

Metallized films include aluminized and silvered Mylar, Teflon, and acrylic. These reflectors are available under many trade names and a wide price range (\$0.75 to \$3.00/ft² projected cost for high volume production). These materials may be used either as front-surface or back-surface reflectors. If used in a back-surface reflector configuration, the polymeric film must be ultra-violet resistant as are acrylic or Teflon. If used in the front surface configuration, the reflective material must be coated or otherwise protected from environmental degradation. Metallized films are frequently laminated to a secondary film for strength, toughness, or backside protection for the metallic surface. The films may be bonded directly to the concentrator structure or to sheet metal for subsequent attachment to the structure.

Major advantages of metallized films are their light weight, availability, and optical properties which allow specular reflectance (for material properly applied) to approach theoretical values for aluminum or silver. Disadvantages include the difficulty of bonding the films to a substrate without "print-through" of anomalies in the bonding agent or surface irregularities; susceptibility of the surface to damage, both from windblown particles and from inadvertent handling mishaps; and the difficulty of cleaning the polymeric surface. Cleaning techniques developed at Sandia Laboratories to date indicate that any mechanical cleaning method causes surface scratching which results in gradually worsening specular reflectance. Various liquid solvent jet methods appear satisfactory except that as-washed specular reflectance values fall below virgin material values by up to 5%.

Silvered Glass. Glass mirrors probably represent the optimum in performance potential for reflective concentrators. High quality, silvered glass in common (2-3 mm) thicknesses can be readily procured for about \$1/ft² in flat sheets. Unfortunately, flat sheets are not of interest to the designers of solar concentrators except for those concepts which employ relatively small flat facets such as the Fixed Mirror Solar Collector, discussed below.

Glass of common thickness can be bent only to very large radii which are applicable to central receiver applications but not to distributed collectors. Glass can be sagged to any shape (including compound) as in windshields and telescope mirrors, but unit costs are high for low quantities because of tooling and labor costs. The automotive industry amortizes tooling and automated production costs over millions of units.

Description of MSSTF

Most of the linear concentrating collectors described have been installed and evaluated at the MSSTF, either in the System Test Facility (STF), or in the Collector Module Test Facility (CMTF).

The STF (Fig. 1) consists of solar collector fields, high- and low-temperature thermal storage facilities, an electrical power generation subsystem, a lithium-bromide absorption air conditioner, an instrumentation and control system, a weather station, and a cooling tower. The STF can produce 32 kWe and about 200 kWth. As an exercise in operating system feasibility, this energy can be supplied to a nearby 1100 m² office building. The STF emphasizes investigation of the integration and performance of arrays (or fields) of collectors, and the interface tradeoffs and control problems of operating all elements of a solar energy plant. For instance, in addition to peak performance tests, comprehensive system-level tests are conducted. Some of these are all-day efficiency, receiver tube losses, vacuum vs. no-vacuum, sun sensor vs. computer tracking, tracking system sensitivity, concentrator surface mapping, automatic defocus, dirt effects, aging effects, parasitic power, fluid control strategy evaluations, early morning startup, parallel collector string control, and pipeline field heat losses.

The CMTF (Fig. 2) obtains thermal and optical performance data for prototype collectors. This facility presently incorporates three separately controlled fluid loops capable of testing three different

FIGURE 1. Midtemperature Solar Systems Test Facility

collectors simultaneously. The three test stations use Therminol-66 heat-transfer oil to 315°C , high-pressure water to 330°C and 18.3 MPa, and low-pressure water to 110°C and 0.51 MPa. This latter loop is

being modified to provide additional capability to test with heat-transfer oils to 425°C.

FIGURE 2. Collector Module Test Facility

The prototype collectors tested at the CMTF may be procured as the result of a DOE-sponsored development contract; may be purchased solely for the purpose of evaluating them to broaden the data base available to designers; or, if mutual benefit can be established, may be provided by industry for testing at government expense. Collectors tested during FY78 include modules from Del-Jacobs, FMC, GE, General Atomic, Hexcel, Itek, McDonnell Douglas, Scientific Atlanta, Solar Kinetics, Soltrax, and Suntec Systems. From 3 to 10 weeks are required to complete testing of a collector module, depending on the weather, the nature of the collector, and the complexity of the test plan. After each test, a report is issued to wide distribution. These reports are assembled into a summary report semiannually.

The primary purpose of all collector tests at the CMTF is to determine the peak performance capability of the collector module from about 150°C to 300°C. The collectors are carefully adjusted and cleaned before testing and are tested at performance

optimized flow rates and at near-normal solar incidence angles. Test sequences are designed to minimize degradation. The efficiencies thus derived may, therefore, be considered to be upper bounds. Of nearly equal importance are thermal loss tests to determine the capability of receiver tube designs. A typical test series may also include tests of "secondary" importance such as all-day efficiency, tracking system performance, effects of turbulence plugs, dirty vs. clean performance, vacuum vs. no-vacuum performance, and various other parametric or off-design tests.

Current Linear Concentrating Collector Technology

Six concentrating solar collectors have been evaluated at the CMTF since August 1977, when refurbishing and expansion of the Facility was completed. Two of these, the SLATS collector by Suntec Systems, Inc. and the Fixed Mirror Solar Collector by the General Atomic Co. (GA) were prototypes of collector field subsystems being designed and fabricated for installation in the Systems Test Facility. Three others--a parabolic trough by the Hexcel Corporation, a parabolic trough by Solar Kinetics, Inc., and a fixed mirror collector by Scientific Atlanta--were purchased as the result of a competitive procurement to buy collectors for evaluation. The sixth collector was a line-focusing Fresnel lens collector by McDonnell Douglas Astronautics Company (MDAC). This collector module was fabricated as the end-item of a complete development contract awarded MDAC to design, analyze, build, and test their Fresnel lens collector concept. The Suntec SLATS collector was tested on the high-pressure water loop, while the other five modules all employ Therminol-66 as a heat-transfer fluid and were tested accordingly.

The General Atomic Fixed Mirror Solar Collector¹ (FMSC) employs a precision cast concrete base configured of 5-cm longitudinal facets arranged along a circular cross section (Fig. 3). Silvered glass strips are bonded to the facets. The concrete base is 7.2 m

long and has an aperture width of 2.6 m. Reflected solar radiation forms a focal line above the concentrator; this line moves on a circular arc with the sun. A movable overhead receiver follows this

FIGURE 3. General Atomic Fixed Mirror Solar Collector

focal line throughout the day. The receiver assembly consists of flattened steel tubing. The receiver is electroplated with black chrome, a "selective" absorptive coating which has high absorptance over the solar spectrum but low emittance to minimize radiation losses. On the back side the tube is insulated with Microtherm, a silica-foam insulation. The receiver features a polished aluminum secondary concentrator extruded to a compound parabolic shape. At the base of the secondary concentrator is a Teflon window to reduce convective losses.

The Hexcel Corporation has developed a parabolic trough collector² which features aluminum honeycomb concentrator structures (Fig. 4). The module tested at Sandia Laboratories

FIGURE 4. Hexcel Parabolic Trough Collector

has an aluminized acrylic film, reflective surface of FEK-163, and an adhesive-backed product developed by the 3M Company for solar application. The concentrator is 7.7 m long with an aperture of 2.6 m and a rim angle of about 70°. The collector is oriented east-west. The honeycomb structure is hinged at the longitudinal axis of the collector to permit some adjustment of the image after installation. The receiver tube is a black-chromecoated steel pipe. The unilluminated side of the receiver is insulated by a double wall cylindrical steel assembly filled with bulk insulation. On the absorbing side of the receiver a non-evacuated glass semi cylinder

interfaces with the steel insulating jacket to minimize convective losses. About 450 m² of an earlier version of the Hexcel collector was installed at Gila Bend, Arizona, in 1977 in a solar irrigation project privately funded by Northwest Mutual Life Insurance Company.

The McDonnell Douglas Fresnel lens collector³ is a prototype of a module which will be deployed in a much larger size--perhaps up to 100 m². The model tested at Sandia (Fig. 5) consists of an aluminum box-shaped structure 5.9 m x 3.6 m x 1.1 m deep. The upper surface of the structure supports four rows of cast-acrylic line-focusing Fresnel lenses. These lenses focus solar radiation on four rows of series-connected receiver tubes mounted in the base of the structure. The receiver tubes are black-chrome-coated steel pipes insulated on the underside by fiber-glass encased in glass cloth "pillows." On the illuminated side the receiver

FIGURE 5. MDAC Linear Fresnel Lens Collector

tube is housed in a polished stainless-steel secondary concentrator. A flat glass cover is also supported by the secondary concentrator and minimizes convective losses. The collector tracks the sun in two axes. A single-post pylon mount similar to that designed by MDAC for their heliostat supports the collector. The cast acrylic lenses were developed and fabricated by Swedlow, Inc.

Scientific Atlanta has adopted a different manufacturing approach to the Fixed Mirror Solar Collector (Fig. 6). Whereas General Atomic bonds their mirror strips to concrete bases, the Scientific Atlanta collector structure is a stamped and riveted sheet metal assembly stiffened by braces. The mirror facets are silvered glass strips 7.6 cm wide and 75.6 cm long. These glass strips are attached to the structure by spring clips. The module tested at Sandia is 9.1 m long and has an aperture 2.1 m wide. The collector is oriented east-west. The receiver is of the line cavity type typical of low rim angle collectors. A flat bank of seven 1.0-cm-diameter black-chrome-coated tubes is installed in a sheet-metal housing. The receiver aperture is glazed with flat low-iron glass installed at the base of a conical secondary concentrator. The unilluminated side of the receiver is insulated to minimize thermal losses.

Solar Kinetics, Inc., has also developed a parabolic trough solar collector.⁴ The concentrator has a 1.3 m aperture, is 6.1 m in length, and has a 90° rim angle (Fig. 7). A two-row array of four such collectors oriented east-west formed the configuration tested at Sandia. The concentrator structure is formed of cast aluminum ribs to which aluminum sheet stock is riveted. The reflective surface is FEK-244 aluminized acrylic film, a later generation version of FEK-163 by 3M Company. The receiver tube is black-chrome coated steel tubing enclosed in a sealed borosilicate glass tube. The glass seal is formed by silicone O rings that make it easier to remove or replace the glass jacket. An evacuation port and valve were incorporated on each receiver so that vacuum effects tests could be conducted. For experimental purposes, a

FIGURE 6. Scientific Atlanta Faceted Fixed Mirror Collector

FIGURE 7. Solar Kinetics Parabolic Trough Collector

variety of receiver tube plugs were provided and evaluated. Whereas most collectors use electric motor drive systems, the Solar Kinetics unit employs a hydraulic system. One advantage of such a system is the rapid slew rates that are possible for emergency defocus in case of coolant loss or flow stoppage. Because of the relative ease of receiver tube assembly, one 12 m string of the Solar Kinetics collector will remain installed at the CMTF to act as a test bed collector in support of the black-chrome process development project being conducted within Advanced Technology Development.

The SLATS collector⁵ by Suntec Systems, Inc., features a Fresnel reflector consisting of movable longitudinal facets (slats) or curved silvered glass (Fig. 8). The module tested at the CMTF was 3.5 m wide by 12.5 m long and consisted of two bays of 10 such slats each 30 cm wide and 3. m long. The individual slats are each set at the proper angle at installation and are linked

FIGURE 8. Suncor SLATS Collector

mechanically to a drive bar so that the sun's reflected image can be continuously focused on a fixed overhead receiver. The bank of slats are tilted southward at about the latitude angle although this tilt can be varied for application tailoring. The slats can be rotated downward when not in operation. This can be an important feature to prevent hail damage and reduce snow, frost, and dust effects. The line-cavity type receiver consists of two parallel steel pipes which are black-chrome-coated and are configured in a counterflow (down and back) arrangement. The tubes are housed in an insulated strongback structure and lie behind a 10-cm glass aperture.

A summary of collector characteristics is presented in Table 1.

CMTF Test Results

Comparative performance data for the above collectors⁶ are presented in Figs. 9 and 10. Figure 9 shows peak efficiency versus receiver outlet temperature. Figure 10 shows thermal loss for each receiver as a function of collector aperture. Receiver thermal

Table 1. Collector Characteristics

Collector	Aperture Area m ²	Secondary Aperture cm	Receiver Length m	Focal Length cm	Geometric Concentration Ratio	Reflector Surface
General Atomic	16.26	13.3	7.16	302.0	43:1	Silvered Glass
Hexcel	15.91	--	6.40	91.4	67:1	FEK-163 Acrylic
McDonnell Douglas	15.54	7.80	17.34	92.7	24:1	Cast Acrylic Fresnel Lens
Solar Kinetics	12.7	--	12.20	26.7	41:1	FEK-244 Acrylic
Scientific Atlanta	18.75	13.3	9.10	248.9	28:1	Silvered Glass
Suntec	35.97	--	12.20	305.0	35:1	Silvered Glass

FIGURE 9. Comparison of Peak Efficiency vs. Temperature for Several Concentrating Collectors

FIGURE 10. Comparison of Receiver Thermal Losses for Several Concentrating Collectors

loss data is not independent of design and cannot be compared as directly as collector efficiency data. Nevertheless, useful information can be provided if the results are not taken out of context.

Although efficiency at 310°C ranges between 34 and 56%, performance is only one of three primary parameters to be considered by designers of solar applications. The other two are procurement/installation cost and long term O&M and repair costs. Also every collector has unique features which may make it preferable for specific applications. Test engineers and designers from each company participated in their test series and without exception each identified areas for design improvements and cost reductions.

STF Collectors

At the System Test Facility, an array of parabolic trough collectors, designed and installed by Sandia, has been in operation since December 1975. Figure 11 is a view of two of the strings of parabolic trough collectors at the STF. The concentrator is a 2.7 x 3.7 m marine plywood structure with a reflective surface consisting of aluminized Teflon bonded to aluminum sheet. Five modules are ganged to form an 18 m string through which the heat-transfer fluid, Therminol-66, flows in series and which operates with a single tracking and drive system. The receiver tubes, carbon steel pipe with black chrome selective coating, are jacketed in an evacuated glass envelope. The 200 m² collector field is arranged in east-west horizontal strings. The output temperature is 310°C.

Considerable data have been accumulated for this system, both in performance testing and in O&M experience.^{7,8,9} Early performance measurements of the collector field indicated peak noon-time efficiencies of slightly more than 50% at 310°C (Fig. 12).

FIGURE 11. Sandia Parabolic Trough Collector Field

FIGURE 12. Peak Efficiency vs. Temperature for Sandia Parabolic Trough Collector Field

Since its initial operation the collector field has accumulated more than 2000 hours of operation at high temperature. Peak efficiency over this time has degraded to slightly under 40% at 310°C . The major causes of this degradation are loss of specular reflectance in the mirror surfaces, loss of absorptance in the black chrome selective surface on the receiver tubes, and moderate warping of the concentrator structure, which has resulted in increasing surface slope errors.

The aluminized Teflon mirror surface is difficult to maintain in near-new condition. Cleaning is a problem because the softness of the Teflon surface precludes mechanical cleaning techniques. Also, the film is easily damaged and any unrepaired surface break develops rapid environmental degradation. Aluminized acrylic films are somewhat more durable. Sandia, Honeywell Corporation, MDAC, and others are conducting outdoor aging tests to determine long-term degradation of a variety of reflective materials.

The black chrome selective coating degrades at temperatures near 300°C. Absorptance losses of 10-12% within a few hundred hours of high-temperature operation have been observed in the Sandia collectors as well as those of several other firms.^{10,6} Absorptance does seem to stabilize after the initial period of degradation.

Both problems are being addressed within the materials and processes task of Application Technology Development Project. Thin glass and sagged glass process developments are being pursued so that silvered glass can economically be applied to parabolic surfaces. Black chrome process control studies are being conducted to determine the sensitivity of electroplating process parameters relative to high-temperature stability.

Other insights gained as a result of collector field operating experience are as follows:

Early morning startup--Getting a solar plant to steady-state design-temperature operation rapidly each day is vital. For a given daily demand, the collector field size is inversely proportional to the number of hours it can be operated at rated output. Factors which delay start-up are the heat capacity of the pipelines, insulation, and receiver tube walls. Adding to the difficulty is the viscosity of most heat-transfer oils (Therminol-66, for instance) when cold.

Tracking and Drive--Computerized tracking may be superior to systems based on sun sensing. A third method, which involves sensing the energy distribution at the receiver and sending error signals to maximize the flux incident on the receiver, shows promise. Drive train design and motor selection are areas in which a wide variety of designs (often bad) are seen. Care must be exercised in design to achieve simple, low-cost mechanical designs and to devise control strategies and select drive motors which minimize parasitic power demands.

Additional Collectors Under Development

The AAI Corporation, of Baltimore, Maryland, has developed a fixed mirror, movable receiver concentrating collector for which they visualize rooftop or other space limited applications. The collector, called the Modular Solar Roof because it is intended to serve as the roof of a building, features a foam aluminum concentrator structure of parabolic cross section. The concentrator structure is faced with aluminum sheet and 5-cm silvered glass strips are bonded to it. The movable overhead receiver has two 2-cm copper tubes with mechanically selective absorbing surfaces. The tubes are installed in an insulated channel structure with a tempered glass aperture. An array of 16 such modules each 2.4 x 9.7 m are presently in operation on the roof of an office building in Disneyworld where they are primarily used to drive an absorption chiller plus a modest winter heating load.

AAI has also developed a linear concentrator of the movable-mirror, fixed-receiver type. The basic module is 2.7 x 10.7 m and contains 32 silvered glass slats, each are 30 x 244 cm. The overhead receiver consists of a black-chrome-coated pipe installed in an insulated channel. A cover glass and a secondary concentrator can be applied or left off depending on the temperature requirements of the application. The bank of mirrors can be tilted to the south or left flat depending on the application. A field of such collectors has been installed at a concrete block plant in Harrisburg, Pennsylvania, under a DOE solar process heat contract. Also, this collector is being modified for use as a water-cooled photovoltaic concentrator. An array of these collectors will be installed at a hospital in Puerto Rico under a recently awarded DOE contract.

Acurex-Aerotherm has also developed a parabolic trough solar collector. A field of these collectors was installed in 1977 at the DOE/New Mexico Solar Irrigation Experiment in Willard, New Mexico (Fig. 13). Acurex is also the prime contractor for the Deep-Well Irrigation Experiment at Coolidge, Arizona, which will be operational

FIGURE 13. Shallow Well Solar Irrigation Experiment at Willard, New Mexico--Acurex Collectors

in 1979. In addition, Acurex has recently completed a solar process heat installation at a Campbell's Soup plant in Sacramento, California, and will soon be starting a 500-kW distributed collector solar power plant in Spain for the IEA. For the Willard irrigation experiment, the collector field is 625 m² and consists of 112 collector modules operating as 14 strings of 8 modules each. The 90° rim angle modules are 1.85 x 3 m in aperture, use Alzak structurally and as the reflective surface, and have a black-chrome-coated, glass-jacketed, non evacuated receiver assembly. The field is arranged in horizontal, north-south rows. The collector field outlet temperature is 215°C. An advanced, higher temperature version of this collector is being designed for the deep-well experiment. A prototype of this collector will be tested at the CMTF in the autumn of 1978.

Del-Jacobs has developed, under contract to Sandia, a small parabolic trough collector featuring sagged silvered glass supported by a structure of stringers and sheet-metal ribs. The concentrator module is 60 cm wide by 240 cm long. The non evacuated, but sealed and desiccated, receiver tube is black-chrome-coated and glass-jacketed. This collector is designed for high-pressure water at 310°C. An array of eight such collectors in two parallel rows (11.5 m^2) will be tested at the CMTF during the summer of 1978.

FMC Corporation has also developed, under contract to Sandia, a novel collector which features a movable stainless-steel belt containing a faceted silvered-glass Fresnel mirror embedded in a pliable adhesive. This concept utilizes handling equipment technology in which FMC has expertise. The concentrator has two degrees of freedom, one being a southward tilt of the entire collector and the other an azimuth track achieved by moving the Fresnel belt along a set of rollers and tracks. A fixed overhead receiver tube absorbs the concentrated solar radiation from the mirror. A small model of this system has been delivered to Sandia and will be tested at the CMTF during the summer of 1978.

Honeywell, Inc., has long been active in solar energy development. Their work has touched on nearly all aspects of material development and collector design--flat plates, troughs, dish collectors and central receivers. One of their early designs, a 120° rim angle parabolic trough, was first placed on test at Desert Sunshine Exposure Test in 1974. The receiver has a selective coating and a glass jacket. A more recent design¹¹ features a concentrator consisting of one-half of a parabola constructed of aluminum honeycomb. The reflective surface is aluminized acrylic film. The selectively coated receiver tube is mounted in an insulated metal housing with a glass window at the receiver aperture. The basic module has an aperture 1.3 m wide by 6 m long. A 1900 m^2 array of these collectors is being installed on the roof of Honeywell's World Headquarters Building in Minneapolis, Minnesota. They will serve the heating and cooling loads of the building.

The Polisolar Company of Switzerland has sold Sandia north-south tilted parabolic trough collectors for evaluation at the CMTF late in 1978. The 21.9-m^2 system to be tested consists of a bank of 12 collectors, each $0.57\text{ m} \times 3.2\text{ m}$. The parabolic troughs are of sheet-metal construction and have a rim angle of 120° . They are installed in a support frame in groups of six modules with common tracking and drive hardware. The reflective surface is sagged silvered glass. The parabolic troughs rotate about a stationary receiver tube. The receiver tube is glass jacketed but non evacuated. A selective absorptive coating is applied. Fluid flow through the system is in series--single pass through each collector.

Collector Costs

Precise costs, particularly projected cost estimates based on assumptions of mass production and the accumulation of production experience, are difficult to address.

The near-term, mid-1980 goals in the national program for solar total energy and small power systems are $\$1000/\text{kW}$ (e+th) and $\$1500/\text{kWe}$ (1976 dollars), respectively, per installed kilowatt of peak power. Solar installations at that cost should be reasonably competitive; and with moderate federal incentives, the commercialization of these solar energy applications can become reality. These goals imply a collector cost of about $\$75/\text{m}^2$.

Currently, several companies are offering fixed-price quotations of $\$160$ to $\$230/\text{m}^2$ not including installation for line focusing collectors in the 300°C performance range.

A recent study¹² on collector evaluation techniques developed a quantifiable feature list and a figure of merit. Contacts with more than 30 companies were made and about 20 responses tabulated. The elements of the figure of merit include annual performance and installed cost. A very interesting unit called a materials figure of merit was also developed. The materials figure of merit is based

on performance and materials cost only. This is a most significant unit because it sets a lower bound on mass-produced costs and properly suggests the powerful influence of lightweight low-cost materials on production costs. Recall the well-known (and possibly overused) rule of thumb that mass produced machinery such as cars and major appliances cost \$1.50 per pound. This study resulted in projections of total costs which ranged between \$150 and \$220/m² including installation, foundations, and interconnecting pipelines. The materials cost projections ranged between \$38 and \$70/m².

Applications

An aggressive, application-oriented strategy is being implemented within the Dispersed Power Systems Program to push solar technology, gain public acceptance, and displace significant quantities of conventional energy as rapidly as possible. In each subprogram a series of DOE-funded system experiments is under way. These will serve to build private-sector expertise, identify technical and institutional problems, and accumulate long-term performance data and O&M experience.

Two Solar Total Energy Large Scale Experiments are in preliminary design. The first LSE is to provide electrical power and thermal energy to a troop housing complex at Ft. Hood, Texas. Westinghouse Electric Corporation has selected a field of line-focusing parabolic trough collectors which will operate at an outlet temperature of 260°C to drive a steam turbine. The second LSE is for a knitwear factory in Shenandoah, Georgia. General Electric has selected a distributed field of two-axis tracking, point-focusing parabolic dish collectors which will elevate the temperature of a heat-transfer fluid to 300°C or 400°C to drive a steam turbine. Strong consideration is being given to constructing in the near future an LSE which features a small central receiver.

The two solar irrigation projects in Willard, New Mexico, and Coolidge, Arizona, have been discussed previously. The shallow-well

experiment at Willard is being expanded in 1978 to include a quarter-section center pivot sprinkler system and a new collector field of about 650 m². The contract for this new field has been awarded to Solar Kinetics who will install an advanced version of the parabolic trough collector described above and tested at the CMTF.

The first Small Power System Experiment is under way. Three system design contracts have been awarded by JPL and site selection is scheduled for late 1978. This project will be for electrical power only and will produce about 1 MW peak. The initial experiment will employ a point focusing collector system--either parabolic dish or central receiver.

A very active photovoltaic concentrator development project is also under way within DOE. The output of photovoltaic cells is approximately proportional to the incident energy density. Therefore, the use of concentrating solar collectors with arrays of solar cells offers the attractive possibility of providing cost-effective solar power plants before solar cell production costs are reduced to competitive levels. The cells must be maintained at relatively low temperatures, which suggests a total energy system possibility in which the coolant for the solar cells could be applied to a nearly thermal load.

A hybrid photovoltaic/thermal experiment to further develop this concept is being constructed at the Mississippi County Community College in Blytheville, Arkansas. The solar concentrators for this application will consist of flat, line-focusing Fresnel reflectors by Honeywell, Inc. The receiver will be lined with solar cells which will be dynamically cooled by water flowing through the receiver tube. The electricity will be used directly or stored in batteries. The hot water will be applied to heating and domestic hot water needs.

A series of industrial process heat experiments, some of which employ concentrating collectors, are being funded by the Conservator

and Solar Applications Division of DOE. The application projects to date serve thermal demands in the 200°C range and below, but the tremendous energy displacement and cost-effectiveness potential for this market is beginning to be appreciated. New initiatives involving larger installations and higher temperatures are being planned.

Some of the existing process heat experiments are listed in Table 2.

Conclusions

A rapidly building data base is becoming available to the designers of solar thermal application projects in the midtemperature range. Solid performance data is available or can be reasonably well predicted for a variety of well-designed and-constructed collectors. Cost projections are becoming more credible although needed high-volume production experience will be forthcoming only as government and privately funded application projects proliferate. Long-term O&M cost experience is crucial. Accumulating this experience cannot be accelerated, but the MSSTF and the wide range of "real world" system experiments involving different hardware concepts, applications, and geographies will help assure adequate breadth of experience. Problems encountered at the MSSTF and other operating application projects are being addressed by Advanced Technology Development and by the other R&D projects within the Solar Thermal programs.

As operating experience grows over the next several years, it will be interesting to observe the place taken in the spectrum of solar applications by each of the basic collector technologies--flat plates, linear concentrating, point concentrating, and central receiver.

TABLE 2

PROCESS HEAT APPLICATION PROJECTS

<u>Contractor</u>	<u>Site</u>	<u>Product</u>	<u>Solar Collector</u>	<u>Operating Temp °C</u>	<u>Solar Use</u>
Honeywell, Inc.	Fairfax, AL	Textile Fabric	1/2 Parabolic Trough Hexcel Concentrator	175	Steam for Cylindrical Drying Rollers
Midwest Research Institute	Lawrence, KA	Alfalfa	Staged-Flat Plates Plus Hexcel Parabolic Troughs	250	Preheat Combustion Air
Acurex Corp.	Sacramento, CA	Soup Can Washing Line	Staged-Flat Plates Plus Acurex Parabolic Troughs	90	Hot Wash Water
AAI Corp.	Harrisburg, PA	Concrete Block Curing	AAI Linear Facet Concentrator/ Fixed Receiver	90	Hot Curing Water

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BUCHMIN INDUSTRIES MANUFACTURERS OF
MIRRORS AND LAMINATED GLASS

by

George M. Jaeger
Buchmin Industries
Reedley, California

Materials: Commercial Mirrors

A. Glass - Sheet - Float - Plate

B. Chemicals Cleaning
 Plating
 Painting
 Face Cleaning
 (D. I. Water)

1) Cleaning

Mechanical:

Brushes, Pads, Cupbrushes,
Rinsing with D. I. Water

Chemical:

Cerium Oxide CeO_2
Other Cleaning Agents

2) Sensitizing the Glass Surface

Mechanical:

Metered Spray Traverse

Chemical:

Stannous Chloride
 $SnCl_2 \cdot 2H_2O$
Hydrochloric Acid

Rinsing with D. I. Water

Silvering

Mechanical:

Metered Spray Traverse

Chemical:

3-Part or 3 Part
Solution

- a) Silver Nitrate
Ammonia
Distilled Water
- b) Rochelle Salt
Distilled Water
(Hydrozine)
- c) Combine with D. I. Water
and Apply

Coat of Silver 0.0001-0.0005 μ m

80 mg/ft²

Copper Backing

Galvanic

Mechanical:

Metered Spray Traverse

Chemical:

Copper Sulphate
Rochelle Salt
Iron Powder
Formaldehyde

Rinse with D. I. Water

Blow Off Water by Air Knives

Preheat

Preheat Glass to 120⁰F
Before Painting

Paints - Mirror Backing

Mechanical:

Curtain Coater, Roller Coater

Chemical:

Solvent Naphtha
Turpentine
Gum Dammar
Red Lead
Zinc White
Cobalt, Manganese

Flash Off Solvents

Bake 250⁰F

Face Cleaning

Iron Chloride
Ammonia
Persulphate

Rinse with Water

Notes

Tests -

Salt Spray Test

150 Hour 300 Hour
20% Saline Solutions

Humidity Test 60⁰C
8 Hour 16 Hour Rest
20 Cycles

Adhesion for Mirrors

Laminated Mirrors

20. A fully automatic conveyor for mirror manufacture

SOLAR CENTRAL RECEIVER
HELIOSTAT DESIGNS

by

C. L. Mavis
Sandia Laboratories
Livermore, California

Abstract

Two generations of heliostats have been developed for the solar central receiver collector subsystem. Heliostats using glass mirrors and heliostats using light weight plastic film mirrors which are protected by a plastic enclosure have been developed. This paper summarizes the design features, and materials used in the two basic types of heliostats. The estimated annual costs for a field of heliostats is also included.

COLLECTOR SUBSYSTEM

The collector subsystem has as its basic function the interception, redirection, and concentration of direct solar radiation to the receiver subsystem. The collector subsystem for a solar central receiver consists of a field of tracking mirrors, called heliostats, and a tracking control system to maintain continuous focus of the direct solar radiation on the receiver. In a 100-MW_e solar central receiver power plant, there can be 15,000 to 25,000 heliostats, depending mostly on the size and the reflectivity of the mirrors.

First-Generation Designs

Figure 1 illustrates the two basic types of heliostats. The Honeywell, Martin Marietta, and McDonnell Douglas designs are examples of heliostats that use a mirror that is exposed to the environment; the Boeing design illustrates the second type in which the reflective surface is an aluminized or silvered plastic membrane that is protected from the environment by a plastic enclosure (dome). The McDonnell-Douglas heliostat concept was selected for the 10-MW_e pilot plant at Barstow, California, which is depicted in Figure 2. A similar artist concept for a field of enclosed heliostats is shown in Figure 3. Each of the first-generation designs shown in Figure 1 was built and tested to verify the designs and point the way for further improvements.

A field of 222 heliostats has been installed at the 5-MW Central Receiver Solar Thermal Test Facility in Albuquerque, New Mexico (Figures 4 and 5). These heliostats were designed for the unique requirements of the Test facility.

Martin Marietta

Boeing

Honeywell

McDonnell Douglas

Figure 2. Barstow Pilot Plant

Figure 1. Boeing Collector Subsystem

Figure 3. A Field of Enclosed Heliostats

Figure 4. Central Receiver Solar Thermal Test Facility Heliostats

Figure 5. Central Receiver Solar Thermal Test Facility Heliostat Field

Second-Generation Designs

Conceptual designs for a second-generation of heliostats have been completed under contracts to the Department of Energy by Boeing Engineering and Construction, General Electric, McDonnell-Douglas Astronautic Company, and Solaramics, Inc. The design goal is to significantly reduce the cost of heliostats as compared to the costs estimated for the 10-MW_e pilot plant at Barstow. Drawings of the four heliostat designs are shown in Figure 6, and a summary of the design characteristics and costs is given in Table I; Table I also lists the Barstow pilot plant heliostat design characteristics and costs.

The major changes that McDonnell Douglas has made to its pilot plant design are (1) increasing the reflective area from 37.5 to 49 m², (2) refining the drive mechanism, (3) replacing the styrofoam core mirror modules with laminated glass, and (4) designing a tapered fit pedestal/foundation and two-part mirror assembly for easy field installation. The projected operations and maintenance (O&M) costs appear to be low, and the annual capital costs for a 100-MW_e field are lower than for all of the other designs, with the exception of the General Electric heliostat. Two areas of concern which remain to be resolved for the McDonnell Douglas design are the life of the mirror edge seal and the possibility of vortex shedding or aeroelastic effects at high wind speeds. The cost estimates at high production rates may be higher than necessary because more vertical integration and improved mass production techniques are believed possible.

Boeing has lowered the cost of their heliostat by replacing the cylindrical enclosure base with a steel dish mounted on stanchions. The enclosure is now a 32-ft diameter, single-piece, polyester dome, blown to a thickness of 0.003

Large Power Systems SECOND GENERATION HELIOSTATS

OBJECTIVES

- Low Cost Mass Production Design
- Detail Cost Estimates
- Broad Industry Participation
- Identify Required R&D

McDONNELL DOUGLAS

SL18231A

BOEING

SOLARAMICS

GENERAL ELECTRIC

Figure G. Second Generation Heliostat
Conceptual Designs

	PILOT PLANT MDAC NTH PLANT	MDAC	BEC	GE	SOLARAMICS
SIGNIFICANT DESIGN FEATURES	STYROFOAM - CORE MIRROR MODULES, INVERTED STOW, PEDESTAL-MOUNTED DRIVES & REFLEC- TIVE UNIT	LAMINATED GLASS MIRROR MODULES, INVERTED STOW, PEDESTAL-MOUNTED DRIVES & REFLEC- TIVE UNIT	ONE-PIECE ENCLO- SURE, DISH BASE WITH 3-PEDESTAL FOUNDATION, RING STRETCHED REFLEC- TOR	ZIPPERED 3-PIECE ENCLOSURE, EARTH- FILLED BAG FOUNDA- TION, OCTAGONAL STRETCH-FRAME REFLECTOR	FOAMED GLASS - MICRO- GLASS MODULES, ONE PIECE CERAMIC PEDESTAL FOUNDATION, PEDESTAL- MOUNTED DRIVES AND RE- FLECTIVE UNIT
REFLECTIVE AREA (M ²)	37.5	49	66	55	38.6
HELIOSTATS/ 100 MW _E	23300	16900	20300	26100	21100
GIMBALED WEIGHT (LB)	3005	3668	366	164	3658
TOTAL WEIGHT (LB) (W/O CONCRETE)	3520	4041	2390	468	5995
NET REFLECTIVITY	.91	.92-.95	.70	.64	.95
CAPITAL COST* (\$/M ²)	95	62	54	27	76
ANNUAL COST** (\$/100MW _E /YR)					
CAPITAL*	8.6x10 ⁶	5.3x10 ⁶	7.6x10 ⁶	4.4x10 ⁶	6.3x10 ⁶
O&M	1.5x10 ⁶	.7x10 ⁶	2.0x10 ⁶	3.0x10 ⁶	.7x10 ⁶
TOTAL	10.1x10 ⁶	6.0x10 ⁶	9.6x10 ⁶	7.4x10 ⁶	7.0x10 ⁶

*250,000 HELIOSTATS PER YEAR, 8% FEE AND 10% CONTINGENCY INCLUDED.

**INCLUDES LAND AND FIELD WIRING

Table I. Second Generation Heliostat Summary Description

inch by a yet-to-be-developed process. The heliostat design has remained essentially the same, although it has increased in size from 48 m² to 66 m². There are several major concerns with this design. First, both the annual capital and total costs for this heliostat are the highest of the four concepts. Second, data on the mechanical and optical properties of the enclosure and reflector plastics are very limited, and the useful life of the plastics cannot be predicted accurately at this time. Third, considerable process development is needed to manufacture one-piece domes. Finally, more vertical integration and mass production methods are needed to lower the cost.

The General Electric heliostat was designed for high volume, low cost production. The three-piece zippered enclosure of 0.003-inch thick weatherized polyester is attached to an earth-filled bag foundation. The heliostat has an octagonal stretch-frame reflector of aluminized mylar and molded plastic drive components. The major concerns with this heliostat are high O&M costs and high technical risk. As with the Boeing design, the optical and mechanical life of the plastics is unknown. Also, the foundation design appears to be especially high-risk, with little cost advantage over other foundation concepts; Sandia recommends a redesign. The General Electric heliostat concept is potentially competitive with the McDonnell Douglas concept at high production rates (250,000 units/year).

Unique features of the Solaramics heliostat include 0.010-inch thick micro-glass mirrors mounted on panels of foamed glass, a one-piece ceramic pedestal set in place with high density urethane foam, and an azimuthal axis which is tilted 23° from vertical away from the receiver. Linear actuators with bell crank mechanisms are used for both azimuth and elevation drives. The design

appears to be cost effective but requires further testing and analysis to verify the cost and reduce uncertainties about the design. Process development is needed for both the foamed glass mirror panels and the ceramic pedestal. The microglass has handling problems, and the mirror module is untested. The drive system with the tilted axis is only a conceptual design at this time and has potentially high backlash and low stiffness. However, the drive system is worth further investigation because of its potential low cost. Finally, production costs of the heliostat can probably be reduced by further use of mass production techniques.

Cost/Performance Analysis

The current basis for heliostat cost and performance comparison is the life-cycle cost of a field of heliostats capable of producing 500 MW_t. It is necessary to use life-cycle costs for a fair comparison because the plastic designs have low capital and high O&M costs, while for the glass designs the opposite is true. It is necessary to use total field cost and performance because the cost (per heliostat) of land and wiring and the energy loss due to spillage and attenuation increase with field size, and the dome-type designs require larger fields. The life-cycle costs are expressed as the uniform (levelized) annual cost of the 500-MW_t field, assuming 30-year life, 11 percent after-tax cost of money, 50 percent income tax rate, 6 percent inflation, and Sum-of-the-Year's-Digits accelerated depreciation. This is intended to simulate a typical utility company's economic analysis.

The results of the cost and performance evaluation are shown in Figure 7. The two glass heliostats are approximately 60 percent cheaper than the plastic designs at the 25,000/year production rate, while at higher production rates the McDonnell Douglas heliostat is about 20 percent cheaper than the nearest

Figure 7. Comparison of Annual Costs of a 500 MW_t Heliostat Field at Different Production Rates for the Prototype Heliostats

competitor. There is considerable uncertainty in these life-cycle cost estimates because they depend on costs derived by four different costing methods, projections from different production scenarios, varying degrees of design maturity, and preliminary performance estimates. Despite the uncertainties, the estimated cost advantage of glass heliostats at the low production rate (25,000/year) is large enough to be considered significant.

For both plastic and glass designs, 60-90 percent of the O&M cost is the cost of washing at the optimum frequency. This cost is greater for the plastic domes because approximately five times as much dome surface area must be washed for a given reflector area. Possible differences in dirt accumulation rates between glass and plastic may alter the differences in O&M costs; however, data are not available at this time.

A Sandia computer code was used to generate a cost-optimal field layout and calculate the annual performance of the field. Different pointing accuracies, receiver sizes, and tower heights were investigated to ensure that the comparison was not biased in favor of any one heliostat design. The results of this effort were the required number of heliostats and the required land area, which were combined with the costs per heliostat and \$1.66/m² (\$6700/acre) for land to yield a total field cost.

Future Development

The conceptual heliostat designs that are designated second-generation heliostats will be developed further in 1979 and 1980. The different design concepts and materials for the major components which might be used on a heliostat with glass mirrors and on enclosed heliostats are listed in Tables II and III respectively. Some of the rationale for the different design choices are also given. Contracts will be let to several successful bidders for heliostat design, fabrication of prototypes, testing and cost estimates.

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<u>COMPONENT DESIGN CONCEPT</u>	<u>MATERIALS</u>	<u>RATIONAL</u>
Foundation		
Poured In-place Pile	Reinforced Concrete	Stability Low Cost
Pre-cast Supported Pile	Pre-stressed Concrete	Low Cost Fast Installation
Support Structure		
Central Pedestal	Galvanized Steel Thinwall Pipe	Strength Weatherability
	Pre-stressed Concrete	Weatherability Fast Installation
Large Drive Wheels	Painted Steel	Large Dimensional Tolerances Reduced Loads
Drive Mechanisms		
Harmonic Drive Linear Screw Drives Conventional Gear Box	Steel	Low Backlash Stiffness
Mirror Support Structure		
Truss Assemblies	Painted Steel	Commercially Available
Roll Formed Steel	Galvanized Steel	Producibility
Wiring and Electronics		
Direct Burial Cable, Electronics in Field	Conventional Cables & Electronics	Low Cost

Table II - DESIGN CONCEPTS FOR HELIOSTATS USING GLASS MIRRORS

<u>COMPONENT DESIGN CONCEPT</u>	<u>MATERIALS</u>	<u>RATIONAL</u>
Mirrors		
Thin Glass, 2nd Surface, Silvered Mirror	Corning Fusion Glass Aluminsilicate Lime Borosilicate	High Specular Reflectivity
Microglas, 2nd Surface, Silvered Mirror	Float Glass Soda Lime	High Specular Reflectivity
Silver w/Protective Covercoat	Silicone	Reflectivity Producibility
Mirror Substrate		
Steel, Polystyrene Sandwich	Galvanized Steel Styrofoam 18	Low Stress in Glass
Steel, Honeycomb Sandwich	Painted Steel Al Honeycomb	Thermal Stability
Foamed Glass	Solaramics Pittsburgh Corning	Thermal Stability Matched Expansion Coefficient Low Stress in Glass
3/16" Float Glass Steel Support	Soda Lime Glass	Producibility Thermal Stability Low Stress in Glass
3/16" Float Glass Edge Support	Soda Lime Glass	Producibility Thermal Stability Low Stress in Glass
Transfer Molded Epoxy Fiberglass	Epoxy Glass	Producibility

Table II - DESIGN CONCEPTS FOR HELIOSTATS USING GLASS MIRRORS (Con't)

COMPONENT DESIGN CONCEPTMATERIALSRATIONAL

Foundation/Dome Support

Buried Soil Filled Plastic Bag.

30 mil Reinforced Polyester

Producibility

Molded Plastic Bowl w/
Concrete Piles

Plastic

Producibility

Support Structure

Steel Pipe

Steel

Rigidity

Al Tubing/Steel Pipe

Aluminum/HSLA Steel, Galvanized

Producibility

Drive Mechanisms

Linear Motors

Molded Lexan Drive Wheel

Producibility
Few Parts
Low BacklashWiring, Electronics,
Blower MotorsDirect Burial Cable Field
Electronics Permanently
Lubricated ac Motors

Conventional

Low Costs

Mirror Support Structure

Stretch Frame

Al Tubing
Steel Wire

Producibility

Folding Frame

Al Tubing

Producibility

Mirror

Stretched Film

Aluminized Mylar (.002" Thick)
Silvered Mylar w/OvercoatLight Weight
High Reflectivity
Light Weight

Enclosure

One Piece Thermoformed Dome,
Zippered Sections, or
Bonded GoresWeatherized Polyester
Polyvinylidene FluorideLow Costs
Weatherability
Low Flammability

Table III - DESIGN CONCEPTS FOR ENCLOSED HELIOSTATS

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PARABOLIC TROUGH CONCENTRATOR DESIGN
FOR SANDIA MSSTF INSTALLATION

Viewgraphs Presented

by

D. V. Sallis

Custom Engineering, Inc.

Englewood, Colorado

PARABOLIC TROUGH CONCENTRATOR DESIGN

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CUSTOM ENGINEERING, INC.

TROUGH STRUCTURE CROSS SECTION

CRITICAL DESIGN REQUIREMENTS

- CONTOUR -- $\pm .030$ INCHES
- SLOPE ERROR -- ONE σ OF $.201^\circ$
- TORSIONAL RIGIDITY -- $.25^\circ$ OVER 12 FEET
- WIND LOADS -- OPERATE IN UP TO 30 MPH
WITHSTAND 90 MPH
- HAIL IMPACTS -- $3/4$ INCH AT 55 FPS
1 INCH AT 65 FPS
- LONG TERM OUTDOOR EXPOSURE
- LONG TERM DIMENSIONAL STABILITY

N5-LBS P5-LBS T5-FT-LBS

1000 750 500 250 0 -250 -500 -750 -1000

Body Loads - 30 mph Wind
12-18-78

ELEVATION ANGLE - DEGS.

30 60 90 120 150 180

TROUGH CONCENTRATOR MATERIALS

<u>MATERIALS</u>	<u>FUNCTION</u>	<u>PROPERTIES</u>
• GLASS	• PROTECT SILVER	• SUNLIGHT TRANSMITTANCE
• SILVER	• REFLECT SUNLIGHT	• REFLECTANCE
• COPPER	• PROTECT SILVER	• CORROSION PROTECTION
• PAINT	• PROTECT COPPER & SILVER	• SEAL AND PROVIDE WEAR LAYER
• POLYESTER	• GROUT	• FILL MISMATCH & PROVIDE STIFFNESS FOR HAIL
• GLASS POLYESTER	• TROUGH STRUCTURE	• ACCURACY & STIFFNESS
• PAINT	• PROTECT STRUCTURE	• WEATHER & U.V. RESISTANCE

AREAS OF CONCERN

- DIMENSIONAL & CHEMICAL STABILITY FOR
LONG TERM OUTDOOR EXPOSURE
- PROTECTION OF THE REFLECTIVE SILVER LAYER
- BONDING TO THE BACK OF THE SILVER COATING
- SAGGED GLASS PRODUCTION CAPABILITIES
- PROCESS DEVELOPED FOR SILVERING OF CURVED
SURFACES
- LONG TERM EFFECTS OF STRAINING OF SILVER
LAYER

SILVER CORROSION

by

W. Abbott

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Columbus, Ohio

Paper or Viewgraphs

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REFLECTOR MATERIALS BY VAPOR DEPOSITION TECHNIQUES

by

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Los Angeles, California

This brief paper has been prepared in response to a request for an assessment of reflector materials. The author does not work with reflector materials per se. However, with his background in metallurgy, materials, and vapor deposition techniques, an attempt is made at addressing some of the pertinent issues in the preparation of the reflecting surface and its protective layer using vapor deposition techniques.

The various components and materials for the same are shown in Table I. Only the substrate, reflective coating and protective layers are considered.

Table II lists the important factors for a reflective system from a materials viewpoint.

Let us examine some of these factors, and consider what is known, not known, and what can be looked into the future. The following remarks are strictly limited to vapor deposited materials with no comparison being attempted with chemically deposited materials.

Composition, Impurities, Imperfections and Alloying/Crystalline-Microcrystalline-Amorphous

The physics textbooks tell us the reflectivity is reduced by interband electronic transitions and electron scattering. It has been observed that a very small amount of impurities can markedly depress the reflectivity of a material. Therefore, an obvious area of theoretical study and predictive analysis is the influence of crystal structure, imperfection content, impurity content, crystallinity/amorphicity, and alloying on reflectivity. It is beyond the writer's expertise to comment on the feasibility of such an analysis. One might even question the value of such a study since the reflectivity of silver is very high ($>95\%$).

Microstructure

Grain size, grain morphology and texture can significantly effect reflectivity. For example, in the case of aluminum, the surface appearance for aluminum coatings can be changed from dull grey to mirror bright by changing the height of surface irregularities from 1.6 to 0.4 microns. This can be accomplished by control of deposition conditions and alloying.

Therefore, the influence of composition, imperfections, alloying (single phase/multiphase microstructure) are important considerations worthy of study. The microstructural variables in thick metallic and oxide coatings have been extensively studied as a function of processing parameters as shown in Figure 1.

It consists of four zones in order of increasing deposition temperature.

Zone 1 Domed macrostructure with "interdome" microporosity ($\approx 500 \text{ \AA}$ wide). Each dome contains very fine grains ($50\text{--}200 \text{ \AA}$ diameter).

Zone T Transition zone, fully dense, fibrous morphology with "chemically weak" interfibre boundaries.

Zone 2 Fully dense columnar morphology.

Zone 3 Fully dense equiaxed morphology.

The presence of higher gas pressures ($p > 10^{-3}$ Torr) increases the transition temperature between zones. The deposition temperature can be the bulk temperature of the substrate or the "equivalent" bulk temperature, i.e. the corresponding atomic surface mobility in the few atom layers at the deposition surface. The latter condition can be produced by deposition in a plasma with a biased substrate thus increasing the kinetic energy of the depositing vapor specie.

It is obvious from the above model that detailed microstructural studies of reflective and overlay coatings as a function of substrate material, surface roughness and deposition parameters is important and essentially unknown.

Corrosion Resistance/Erosion Resistance

Due to the long service periods, 30 years, the pronounced susceptibility of silver to tarnishing as well as the need for protection from the erosive wear of sand particles, an overlay coating on the reflective surface is very important, particularly for front surface mirrors. A number of sprayed polymers applied by spraying, dipping and overlay have been tried with fairly good results in some cases (Ref. 1). On the other hand, there is considerable promise that thin transparent, wear resistant, pinhole free oxide coatings can be deposited by Physical Vapor Deposition techniques (evaporation, sputtering, and ion plating).

Obviously, adhesion of the reflective coating to the substrate and the overlay coating to the reflective coating is very important. Again good adhesion can be readily obtained with PVD techniques properly used. A common misunderstanding is the failure to differentiate between adhesion and fracture. One may get good adhesion but the coating may fracture in the coating or in the substrate due to residual stresses.

What PVD Can Do Today

PVD Technology can:

1. Deposit metals, alloys, compounds, mixtures thereof

2. Deposit them at high rates up to 250,000 Å/minute
3. Deposit materials on a variety of substrates at compatible deposition temperatures
4. Replicate the surface finish of the substrate

PVD technology is used on a large scale today for various coating requirements. The one closest to the present discussion is the coating of multiple metal and/or oxide layers on large pieces (up to 12 ft. x 14 ft. moved vertically) by electron beam evaporation at a throughput of 300 ft per minute. Smaller pieces of glass are coated by sputtering with the glass being horizontal.

On fairly large systems, coating costs are rumored to be \$10/square meter which can be further scaled down.

The overall costs can be significantly effected by an integrated approach where the glass is produced and coated in an in-line system,

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TABLE I COMPONENTS AND MATERIALS

COMPONENTS

CURRENT AND POTENTIAL MATERIALS

SUBSTRATE

GLASS

A. FLOAT GLASS (LOW IRON FOR BACK SURFACE MIRRORS)

B. MICROGLASS (POSSIBLY ON A FOAM GLASS BASE)

POLYMERS

POLISHED ALUMINUM

REFLECTIVE COATING

SILVER BY VAPOR DEPOSITION OR CHEMICAL DEPOSITION

ALUMINUM BY VAPOR DEPOSITION

ALLOYS: Ag-Al, Ag-Al-X

BERYLLIUM (UNLIKELY FROM COST, AVAILABILITY AND TOXICITY
VIEWPOINTS)

TITANIUM

PROTECTIVE LAYER

GLASS

ALUMINUM OXIDE (BY VAPOR DEPOSITION)

OTHER OXIDES

POLYMERIC COATINGS (REF. 1)

TABLE II IMPORTANT FACTORS FROM MATERIALS VIEWPOINT

COMPOSITION - PURE MATERIAL, IMPURITIES, ALLOYING

MICROSTRUCTURE - GRAIN SIZE, GRAIN MORPHOLOGY, TEXTURE

CRYSTALLINE OR (MICROCRYSTALLINE) AMORPHOUS

OPTICAL PROPERTIES - REFLECTIVITY

CORROSION RESISTANCE - ENVIRONMENT, TIME

EROSION RESISTANCE - ENVIRONMENT, TIME

ADHESION OF VARIOUS LAYERS

SURFACE PREPARATION - ROUGHNESS

EFFECT OF PROCESS PARAMETERS ON ABOVE -

DEPOSITION TEMPERATURES, RATE, ENVIRONMENT

DEFECTS IN COATINGS

DURABILITY OF ADHESIVES AND SEALANTS

by

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DURABILITY OF ADHESIVES AND SEALANTS

INTRODUCTION

Many potential designs for parabolic, dish, or heliostat Solar Concentrators will utilize adhesives or sealants as a part of the design.

The major requirements of adhesive/sealant systems will be to maintain the structural integrity of the panels, eliminate unwanted dimensional changes of the reflecting surface and eliminate any form of attack on the metal vapor coated surface which would reduce or alter it's reflectivity.

The long term exterior durability of such bonded and/or sealed systems will be of prime importance to this new industry. These units will be expected to withstand up to thirty years or more of rigorous exposure to the elements and the adhesives or sealants must display exceptionally good water resistance, ultraviolet light resistance, low moisture vapor transmission, and resistance to thermal cycling among other requirements. These are not new requirements since good exterior durability of bonded or sealed joints has been a requirement of adhesive and sealant systems in other industries for many years. They have developed test methods and specifications that could very well serve as guide criteria for evaluating materials for Solar Concentrator usage.

This paper is directed at identifying, in a general way, factors that affect bondline or sealant joint durability and enumerating pertinent and potentially applicable test methods currently being used. In addition, typical properties of specific types of adhesives and sealants, as they might relate to potential uses in the construction of Solar Concentrators are also discussed.

DISCUSSION

- I. Factors Affecting Adhesive/Sealant Durability: Several diverse factors such as substrate type, surface preparation, surface treatment prior to bonding (etching, priming, etc), joint design, degree of sustained load, modulus of elasticity of the adhesive/sealant, the thermal cycling the bond or joint undergoes, all affect the durability of a bonded system. Other factors that are important are the effect liquid water as well as high humidity have on the bondline or joint; its' resistance to UV light and ozone degradation; and resistance to corrosion producing environments

(ie salt spray or oxides of sulfur). A few of these factors are highlighted below.

A. Surface Preparation

Since either initial or long term strength of an adhesive bondline is determined primarily by the physical and chemical properties of the adhesive/adherend interface, good surface preparation is extremely important in obtaining durable bonds. This may include special cleaning, abrading, etching, and/or priming. Likewise, sound, clean, perhaps primed, joint substrates give optimum long term sealant performance.

B. Joint Design

Joint design is one of the most important considerations that affects initial bond strength, as well as durability of structurally bonded joints. Joints are stronger in tension and in shear strength than they are in peel or cleavage. This must be taken into consideration in designing any bonded structure.

The joint width/depth ratio, as well as total joint movement expected over the service temperature range encountered, is of paramount importance in designing a joint to be sealed. It is important that these criteria be seriously considered in an early design stage rather than freezing on a design then attempting to bond or seal as an "after thought". Optimally designed sealer joints, have a width of at least twice the joint depth and exhibit total joint movement of $\pm 12.5\%$ of the joint width or less.

C. Modulus of Elasticity - Adhesives

Where there are large differences between the coefficients of expansion of dissimilar adherends, it is often quite beneficial to use an adhesive of lower modulus (displaying increased flexibility or elongation) as a stress relieving interlayer to increase bond permanance during thermal cycling.

An example of a forgiving type of an adhesive in this type of an end use would be two part room temperature curing urethane adhesives.

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II. Potential Failure Modes

A. Adhesives

Adhesive bonds fail for a variety of reasons, ie; (1) Wrong adhesive chosen, ie lack of flexibility, etc. (2) Lack of initial adhesion -due to poor surface preparation, insufficient wetting of the substrate prior to cure (3) Subsequent bond degradation due to undercutting by water or chemicals, UV light exposure (particularly on transparent substrates) or embrittlement or reversion due to thermal cycling. (4) They may also fail due to attack of the adherend interface by corrosive ingredients contained in the adhesive itself.

B. Sealants

Sealant joints likewise, fail for a number of reasons and among them are:

1. Improper sealant chosen, ie. one having excessive shrinkage during cure or drying step, inadequate initial flexibility; inadequate water or MVT resistance, poor recovery characteristics etc.
2. Poor application technique leaving voids in joint.
3. Poor joint design giving excessive joint movement resulting in loss of adhesion or sealant tearing.
4. Poor aging properties such as hardening or reverting during weathering, or loss of adhesion to substrate due to corrosion or undercutting.

III. Potentially Helpful Existing Sources of Information

A. Adhesives

1. Electrical Industry - This industry has bonded and coated copper for many years. Good adhesion to copper as well as non attack of copper is important to them. There are many established test methods that might be relatable to bonding to copper vapor coating over silvered glass in the Solar Concentrator field. One such test that measures copper corrosion is ASTM D 3482-76 entitled "Determining Electrolytic Corrosion of Copper by Adhesives".
2. Aerospace Industry - The aerospace industry has been the driving force in emphasizing the need for improved structural adhesive durability systems and test techniques. Many

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test methods have been developed, most of which are based on exposing adhesive bonds to high humidity with some mode of stress applied to the bond area. This has provided a means to evaluate and rank adhesive systems with respect to their durability. 3M Company has been a leader in this field.

B. Sealants

1. Insulated Glass Manufacturers. Low moisture vapor transmission, low outgassing, good adhering, very weatherable sealants have long been a requirement in this industry. These properties are also of prime importance in sealing Solar Concentrators. The Sealed Insulated Glass Manufacturers Association (SIGMA) should be a prime source of information. Over twenty years of sealed window unit durability has reportedly been achieved by some window manufacturers.
2. Construction Sealant Industry. Very durable exterior grade sealants are important to this industry. There are test methods for Building Sealants such as those found in the American Standards Association A-116.1 specification and Federal Specifications TTS-00230 and TTS-00227 which could be drawn upon in formulating test criteria for Solar Concentrator panel sealants.
3. Automotive Windshield Sealing Industry. All major auto manufacturers have specifications covering windshield sealers which are permanently rubbery, display good adhesion and exhibit good long term weathering properties. These specifications are a good background resource. A typical specification is Ford's ESB M3G95A.

IV. Typical Sealant Properties

The following three charts describe typical properties of some of the major types of commercially available, higher performance, liquid and solid sealers. Although all of these types of sealants have been used extensively in exterior applications, substrate compatibility (ie non attack of silver, copper, or aluminum reflective vapor coatings), optimum weatherability, and low moisture vapor transmission will probably be the deciding factors in the final

choice of sealants for various concentrator panels. It may well be that sealant combinations will need to be used on each type construction such as in the primary/secondary seal concept used in the insulated glass industry. It is of particular interest, that the compressible polyisobutylene or butyl solid sealers display superior weathering as well as having very low moisture vapor transmission rates.

TABLE 1

A COMPARISON OF GENERAL PROPERTIES OF SEVERAL TYPES OF LIQUID SEALERS

(A RATING OF 1 IS EXCELLENT AND A RATING OF 5 IS POOR)

	<u>POLYSULFIDE</u>		<u>ACRYLIC</u>	<u>SILICONE</u>	<u>POLYURETHANE</u>		<u>BUTYL</u>
	<u>ONE PART</u>	<u>TWO PART</u>			<u>ONE PART</u>	<u>TWO PART</u>	
1. ADHESION WITHOUT PRIMING	2	2	1	4	4	4	2
2. CURE RATE	5	1	4	2	3	1	4
3. SHRINKAGE	1	1	2	1	1	1	3
4. WEATHERING	3	2	3	1	3	3	2
5. WATER RESISTANCE	1	1	5	1	1	1	1
6. MOISTURE VAPOR TRANSMISSION RATE.	2	2	4	4	5	5	1
7. LOW TEMPERATURE FLEXIBILITY	2	2	5	1	2	2	2
8. HEAT RESISTANCE	3	2	4	1	3	3	2
9. RECOVERY	3	2	5	1	1	1	4
10. LOW STRESS ON BOND LINE (LOW MODULUS)	3	1	1	4	4	2	1
11. LENGTH OF FIELD HISTORY	3	1	2	2	5	3	2

TABLE 2

3M SOLID SEALERS - COMPARISON OF PROPERTIESA RATING OF 1 IS EXCELLENT AND A RATING OF 5 IS POOR

	Non-Drying Poly- butene Base	Compressible Polyisobutyl- ene Base	Reinforced Butyl Rubber Base	Compressible Butyl Rubber Base
1. TACK	1	4	3	1
2. EASE OF COMPRESSION	1	3	4	2
3. WEATHERING	2	1	1	1
4. SHEAR STRENGTH	5	3	2	2
5. SOLVENT RESISTANCE	5	5	4	4
6. DIRT PICK UP	5	2	2	5
7. RESISTANCE TO STATIC LOAD	5	4	2	2
8. M.V.T.	3	1	1	1
9. ELEVATED TEMPERATURE STRENGTH				
A. SHEAR	5	5	2	2
B. COMPRESSION	5	5	2	2
10. RECOVERY	5	5	2	2
11. BLEEDING	3	1	1	1
12. WATER RESISTANCE	3	1	1	1

TABLE 3

SEALERS - MOISTURE VAPOR TRANSMISSION RATES
(per ASTM E-96-66 Procedure A)

<u>SEALER TYPE</u>	<u>GRAMS/METER² /24 HRS.</u>
3M Polysulfide Base	
Two Parts	1.68-4.00
One Part	1.92
3M Polyisobutylene Base	0.32
3M Butyl Rubber Base	0.21
One Part RTV Silicone	14.17
3M Two Part Silicone	9.53
3M Flexible Epoxy-2 Part	2.32

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V. Durability Data - 3M Structural Adhesive Systems.

The attached table 4 describes unaged, overlap shear strength data of 250°F curing one part epoxies, 2 part room temperature curing epoxy polyamides, as well as 2 part room temperature curing urethanes on metal substrates.

Extended durability testing has been performed on these systems. Test specimens as described in Figure 1 were prepared, placed under various stress levels in spring loaded fixtures, and subjected to 100°F/100% relative humidity in an environmental chamber and tested until the bonds broke.

Results are tabulated in Figures 2, 3, 4 and 5. These graphs are interpreted as follows. The darkened bar graph indicates failure. The light bar graph with the arrow indicates no failure through that time period. The letters adjacent to the failure bar graphs indicate the type of failure, ie., C stands for cohesive failure, A for adhesive failure, AP for adhesive to primer failure and CP for cohesive failure of primer. Figure 6 illustrates a typical failure mechanism.

TABLE 4

		Control Strength at Environment Temp. (100°F)	
		5052T-4	
<u>Category</u>	<u>Chemistry</u>	<u>Bare Aluminum</u>	<u>1010 C.R. Steel</u>
<u>250°F Cure Paste</u>			
EC-2214 HT	Epoxy/Amine Cure	1580 psi	
EC-2214 HD	Nitrile/Epoxy	2522 psi	2482 psi
XA-3430	Vinyl/Epoxy	2040 psi	2337 psi
EC-3455	Polyether/ Epoxy	3556 psi	2555 psi
<u>2 Part RT Cure Epoxy (BPA Epoxy/Polyamide)</u>		<u>5052T-4 Bare Aluminum</u>	
EC-2158 B/A	Filled	1577 psi	
EC-2216 B/A	Flexible	2220 psi (1439 psi EC-1945)	
EC-2054 B/A	Al. Filled	2497 psi	
EC-1838 B/A	Chrome Oxide Filled	2422 psi	
EC-1751 B/A	Al. Filled	2135 psi	
EC-1945 B/A	Non Sag Primer/Chromate	-	
		<u>5052T-4 Bare Aluminum (EC-1945 Primed)</u>	
<u>2 Part RT Cure Urethanes (Isocyanate/Polyol)</u>			
EC-3529 B/A	6-8 Min. Worklife	1275 psi	
EC-3539 B/A	6-8 Min. Worklife	1232 psi	
EC-3532 B/A	6-8 Min. Worklife	1893 psi	
EC-3535 B/A	2-4 Min. Worklife	2002 psi	

3M SUSTAINED LOAD DURABILITY TEST

FIGURE 1
6-30/76

Test Specimen

Figure 2

**250°F CURE PASTE ADHESIVE
SYSTEMS
5052T4 Bare Al—FPL Etch**

Figure 3

Figure 4

**TWO PART RT CURE
EPOXY SYSTEMS
FPL Etch 5052T48ARE AL**

Figure 5

**TWO PART RT CURE
URETHANE SYSTEMS
FPL ETCH 5052T4 BARE AL**

Figure 6

FAILURE MECHANISM

Durability of Adhesives and Sealants

In conclusion, we can make the following statements concerning structural adhesive durability.

1. Heat curing systems possess greater durability than RT cure systems.
2. Surface preparation is an important factor and it is emphasized again, that systems must be evaluated on the same surface preparation to obtain valid comparisons.
3. The chemistry of adhesive systems does have an effect on durability and highly crosslinked systems generally possess better durability.
4. Materials, such as vinyl polymers, which can break down to form HCL are detrimental to durability.
5. The use of chromate pigmented primer systems greatly enhances durability.

As can be seen, many things influence the durability of adhesive bonded joints. It is, therefore, recommended that a durability test be conducted on all systems before they are selected for any application. This includes the adherends, surface preparation, adhesive and cure parameter needed for each application.

It should be noted, that while this durability technique can certainly be used to rank the stress bearing capabilities of adhesives, the correlation of this test data to actual service life is yet to be determined. Many of the adhesives studied, even those which appear poorer by this technique, have been in service for several years with good performance in many applications.

DETERIORATION OF SILVERED GLASS MIRRORS
FOR USE IN SOLAR ENERGY SYSTEMS

by

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Introduction

Degradation of the silvering on the mirror modules was first noticed on a Sandia 2-inch, styrofoam core module that had been mounted on the McDonnell-Douglas (MDAC) heliostat at Sandia, Livermore. The degradation consisted only of streaking and/or speckling (see Figure 1). An intensive program was immediately started to try to duplicate this degradation in the laboratory and to analyze the adhesive, sealant, silver surface, and the fluid found in the module between the glass and a styrofoam core. A survey of the severity of the problem was also begun in order to assess its magnitude and to provide a baseline for measuring additional degradation. The modules investigated were:

SANDIA modules (fabricated per SAND78-8269)
McDonnell-Douglas modules
Martin-Marietta modules at SLL and in Maryland
Honeywell modules at SLL and in Florida

The findings are summarized below according to module fabrication.

SANDIA Modules:

Ten modules were examined very closely for any sign of deterioration. The module with the most damage had been mounted on a working heliostat from February to October (see Figure 2 for module construction). The deterioration covered an area of approximately 10% of the total area. The deterioration was not continuous and was only observed at one end of the module. It consisted of speckling and streaking. Sandia modules mounted on a wooden frame for outdoor exposure since August show very little or no deterioration. At present we feel this is because of the more limited outdoor exposure. All mirror modules were made from 1/8-inch low iron float glass silvered by Buchmin Industries.

MDAC Modules:

Ten modules located at Sandia, Livermore were examined (5, 2-inch and 5, 4-inch modules). In almost every case the deterioration followed a definite pattern (see Figures 3 to 7) which may be attributable to adhesive bond lines between 4 styrofoam panels used to make the module core, (see Figure 8 for module construction).

Another type of deterioration -- which looks like water droplets between the glass and silver -- is actually spots where the silver is separating from the glass. All MDAC modules used mirrors from the same lot as the Sandia modules.

MMC Modules:

Eleven modules were examined. Nine are at Sandia, Livermore and two are at MMC facility near Baltimore, Maryland. The modules at Sandia were constructed with the same mirrors as the Sandia modules but with an aluminum honeycomb core faced with sheet steel (see Figure 9). In some cases at Sandia, the deterioration seemed to follow the adhesive bond line. The deterioration consisted of large ($\sim 1\frac{1}{2}$ - $2\frac{1}{2}$ inches in diameter) dark

rings (Figure 10) and some speckling. The modules located in Maryland showed very little silver degradation, although some suffered massive fractures. These modules used mirrors made by Gardner.

Honeywell Modules:

Twelve modules were examined. Four are at Sandia and eight are at a Honeywell facility in St. Petersburg, Florida. These modules had an aluminum honeycomb core faced with sheet steel and a thin urethane foam sheet reinforced with aluminum honeycomb onto which the glass was mounted (Figure 10). There was some streaking and speckling and a pattern that indicated that the aluminum in the aluminum honeycomb reinforced backing was contacting the mirror and enhancing silver deterioration. These modules used mirrors made by Carolina. It has also been reported that some minor deterioration has been observed on mirrors exposed at Desert Sunshine Company in Arizona for 32 weeks at a solar concentration of 8 suns.

Analysis and Experiment

Thickness and uniformity measurements of the paint and metal coatings were completed on four samples from the same Buchmin mirror. The silver layer varied from 56.6 mg/ft² to 82.5 mg/ft² with an average coverage of 66.0 mg/ft². The copper layer varied from 35.3 mg/ft² to 48.3 mg/ft² with an average coverage of 41.1 mg/ft². The specified coverage for these mirrors was 70 to 95 mg/ft² of silver and 20 to 25 mg/ft² of copper.

Accelerated aging tests were conducted on mirror samples with and without adhesive subjected to four environments at two temperatures: at 65°C, 1) control 2) water only 3) water + 1% isopropyl alcohol and 4) water + an unknown dilution of water soluble extract from the sealant used in the modules; at 77°C, water + 1% isopropyl alcohol. The isopropyl alcohol was intended to substitute for the alcohol that was detected in the moisture found between the mirror and styrofoam core in a severely deteriorated Sandia module.

After 450 and 625 hours at temperature all of the samples layered with adhesive showed greater than 30% degradation over the area covered by the solutions (Figures 12 and 13). Those samples not covered with adhesive showed less than 5% deterioration. At the conclusion of the tests the samples will be analyzed to compare with the analyses on mirror samples from the modules.

Summary

The severity of the problem is apparent. Chemical and surface analyses have been done at Sandia, Livermore. Although the results are inconclusive, the studies are continuing with the hope of identifying a solution that can be used in the near future.

It appears that the problem may be eliminated by using a thicker layer of paint. Analyses of a mirror made by Schott in Germany shows a much tougher paint layer. It has two coats of paint; a copper loaded paint and a gray backing paint. The copper layer is about 16 mg/ft² and the silver layer is about 85 mg/ft². After accelerated aging equivalent to 6 years

outdoor exposure the mirror shows virtually no degradation.

FIGURE 1. STREAKING AND SPECKLING

FIGURE 2. SANDIA STYROFOAM CORE MIRROR MODULE

FIGURE 4. MDAC 4" MODULE S/N 020
1 DEC 78

FIGURE 5. MDAC 4" MODULE S/N 019
11 DEC 78

FIGURE 3. MDAC 2" MODULES S/N
027, 014, 011, 013, 08 (TOP
TO BOTTOM) 17 NOV 78

TAPE LINES INDICATE DETERIORATION

FIGURE 6. MDAC 4" MODULE S/N 015
11 DEC 78

FIGURE 7. MDAC 4" MODULE S/N 016
11 DEC 78

TAPE LINES INDICATE DETERIORATION

SANDIA DESIGN

MDAC DESIGN

FIGURE 8. MIRROR MODULE EDGE CAP CONFIGURATION
(ONLY DESIGN DIFFERENCE)

FIGURE 9. MARTIN-MARIETTA MIRROR MODULE

FIGURE 10. MMC MODULE

11/28/78

TAPE LINES INDICATE DETERIORATION

FIGURE 11. HONEYWELL MIRROR MODULE

FIGURE 12. SAMPLE FROM ACCELERATED AGING TESTS

FIGURE 3. SAMPLE FROM ACCELERATED AGING TESTS

WEATHERING AND LEACHING OF GLASS
FOR SOLAR HELIOSTATS

by

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SOLAR TRANSMITTANCE OF OLD GLASS

In order to assess the effects of weathering on the transmittance of glass, several old samples were collected from two desert environments for evaluation. The glass obtained by PNL at the Hanford reservation in Washington came from south-facing, vertical windows which were known to be over forty years old. The glass obtained by Sandia from Barstow, California is estimated to be over twenty years old (S. Roche, personal communication).

The samples all contained areas that were covered from exposure by the window framing material. It was thus possible to compare the exposed and presumably unexposed areas of the glass. Table 5 lists the various values of the solar transmittance of unexposed glass as T_s . The relative difference in transmittance of the exposed areas is given as ΔT_s .

TABLE 5. Solar Transmittance of Weathered Glass

	<u>T_s (Unexposed)</u>	<u>ΔT_s (Exposed)</u>
HANFORD GLASS		
Sample A	0.865	-0.019
Sample B	0.864	-0.022
Sample C	0.839	-0.007
Sample D	0.861	-0.001
BARSTOW GLASS		
Sample A	0.900	+0.005
Sample B	0.841	+0.011
Sample C	0.845	+0.005

The differences between the exposed and unexposed areas are generally less than two percent. The spectral transmittance of the exposed areas of all the samples measured was characterized by a fairly large loss of transmittance in the UV-visible and an increase in the near infrared. Although the specularly of the samples was not measured, visually they all appeared

fairly clear and free of surface contamination and abrasion. The only definitive conclusion that can be drawn from the scattered data is that the effects of weathering appear to be small.

One of the Hanford samples (D) was more carefully characterized in order to determine if the changes in the solar transmittance were due to surface or bulk effects. SEM micrographs were taken of both the exposed and unexposed areas to look for changes in the surface morphology. Some differences were observed but nothing extreme. The exposed area away from the frame edge has a slightly rougher surface texture than the unexposed area. The area immediately adjacent to the frame edge showed significant texture. This is possibly due to additional leaching of the glass from longer moisture contact near the frame edge.

In addition, normal hemispherical reflectance and transmittance measurements were performed. The results are shown in Table 6. Although there was very little change in the specular transmittance, the hemispherical transmittance of the exposed area increased markedly. Both the solar reflectance and absorptance decreased correspondingly.

TABLE 6. Solar Weighted Optical Parameters for the Hanford-D Glass Sample

	<u>Specular Transmittance</u>	<u>Hemispherical Transmittance</u>	<u>Hemispherical Reflectance</u>	<u>Calculated Absorptance</u>
Unexposed	0.861	0.860	0.067	0.073
Exposed	0.860	0.891	0.055	0.054
Change	0.001	+0.031	-0.012	-0.019

The spectrophotometer curves which have been corrected for offset and gain are shown in Figures 1-3. The difference curves are also included. The hemispherical, like the specular, transmittance is characterized by an increase in transmittance in the exposed area in the near infrared and a decrease in the blue. The crossover point is shifted from about 700 nm for the specular curve to about 480 nm for the hemispherical curve.

FIGURE 1. Specular Transmittance of the Hanford-D Glass

FIGURE 2. Hemispherical Transmittance of the Hanford-D Glass

FIGURE 3. Hemispherical Reflectance of Hanford-D Glass

The broad Fe^{2+} absorption band at 1100 nm has diminished in intensity in the exposed area. The magnitude of the reflectance decrease at 1100 nm is not sufficient to account for the transmission increase. It is therefore reasonable to assume that the concentration of Fe^{2+} has decreased. It has been suggested that solarization could raise the oxidation state of the iron from the 2+ to the 3+ state, thus increasing the absorption around 380 nm. Although the data support this thesis, the results are not conclusive. Further measurements are required to determine the exact mechanisms for the observed changes. It is clear, however, that changes in transmittance are due to both surface and bulk effects.

DURABILITY OF GLASS

To determine the durability of glasses proposed for heliostat mirrors, selected samples were leached in a Soxhlet apparatus and pH 4 and pH 9 buffer solutions. The glass samples produced by the float process are soda-lime-silica glasses, whereas the glass samples produced by the fusion process are aluminosilicate glasses.

Two basic types of sample configurations are used. One was a piece of the "as-received" plate cut $\sim 1/2 \times 1/2$ -in. The other type of sample consisted of crushed glass plate, screened to -40 + 60 mesh (U.S. Standard). The crushed glass has greater surface area than the plate sample (200-300 cm²/g vs 2-4 cm²/g) and thus is used for obtaining accelerated results.

The Soxhlet test operates at 95°C and the sample, which is contained in a stainless steel bag, is exposed to redistilled water every 3 min., as illustrated in Figure 13. The pH 4 buffer solution is made from ammonium hydroxide and ammonium chloride and the pH 9 from sodium acetate and acetic acid. The pH 4 and pH 9 tests are at room temperature and the sample is contained in a stainless steel bag. The solutions are contained in plastic bottles which are agitated by a shaker machine.

The Soxhlet test is an accelerated test that is useful for general comparison and ranking of glasses. This test is not characteristic of heliostat environmental conditions. The room temperature, pH 4 and pH 9 buffer leach tests may be more representative of actual heliostat conditions. These tests simulate the attack of acidic or basic environments under static conditions.

There are two general mechanisms of corrosion or leaching of solids. The first follows the square root of time, $t^{1/2}$, and represents a region of selective ion leaching and silica gel formation. The second leaching mechanism has kinetics directly proportional to time, t^1 , and represents dissolution of the silica gel region and/or bulk leaching. Since only one

FIGURE 13. Soxhlet Leach Test Apparatus

or two time periods were used in this study, conclusions cannot be made concerning leaching mechanism or region.

The results of the durability tests are presented in Tables 7 and 8. These results are expressed both as a percent weight loss and as weight loss per cm^2 per day ($\text{g}/\text{cm}^2\text{-d}$). The latter is useful to predict penetration into the glass surface if one is in the bulk leaching region. For example, $10^{-5} \text{ g}/\text{cm}^2\text{-d}$ would correlate to a penetration of $3.9 \times 10^{-6} \text{ cm/day}$, assuming density of $2.54 \text{ g}/\text{cm}^3$ under a bulk leaching mechanism.

In general, the aluminosilicate glasses were much better in Soxhlet and pH 9 environments than the soda-lime-silicates. All glasses were equal in pH 4 buffer solutions. It appears that the twin-ground plate glass may have better leach resistance than the float glasses. This may be due to slight compositional differences as well as surface condition.

SEM micrographs were obtained on the low iron float plate samples 5 and 6 for "as-received" reference (both sides), Soxhlet (both sides), pH 4 (both sides), and pH 9 (both sides), as illustrated in Figures 14-16. No surface effects could be observed on the "as-received" pH 4 and pH 9 samples. Ridges or surface intersections were observed on the Sn side of the Soxhlet sample. The atmosphere side of the Soxhlet sample contained numerous "bumps" or particles which appeared to be from the bulk of the glass (i.e., not a leach product). The Sn side was identified by UV fluorescence and energy dispersive X-ray analysis as shown in Figure 17.

SEM micrographs of representative areas of crushed Soxhlet particles of the low iron float glass sample 6 are shown in Figure 18. Some regions had a "sponge" surface texture whereas others had a smooth surface. The "sponge" texture was not observed on crushed Soxhlet leached samples of aluminosilicate glass. The high weight loss of the crushed float glass samples correlates with the observation of a "sponge-like", probably high silica, gel surface layer.

TABLE 7. Leachability of Ground Glass Samples^(A)

SAMPLE	SOXHLET 72 HR		pH9				pH4			
			24 HR		120 HR ^(B)		24 HR		120HR	
	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D
1 FLOAT	23.77%	4.0×10^{-4}	0.15%	7.5×10^{-6}	0.18% ^(D)	1.8×10^{-6}	0.05%	2.5×10^{-6}	0.05%	5.0×10^{-7}
6 FLOAT-LOW IRON	22.53	3.8×10^{-4}	0.31	1.6×10^{-5}	0.41	4.1×10^{-6}	0.04	2.0×10^{-6}	0.04	4.0×10^{-7}
4 FLOAT	28.35	4.7×10^{-4}	0.15	7.5×10^{-6}	0.25	2.5×10^{-6}	0.02	1.0×10^{-6}	0.34 ^(D)	3.4×10^{-6}
12 TWIN GROUND	9.64	1.6×10^{-4}	0.08	4.0×10^{-6}	0.21	2.1×10^{-6}	0.10	5.0×10^{-6}	0.10	1.0×10^{-6}
7 FUSION	1.08	1.8×10^{-5}	0.02	1.0×10^{-6}	0.04	4.0×10^{-7}	0.06	3.0×10^{-6}	0.06	6.0×10^{-7}
13	1.78	3.0×10^{-5}	0 ^(C)	0	0.03	3.0×10^{-7}	0.05	2.5×10^{-6}	0.05	5.0×10^{-7}

(A) SCREENED TO -40 + 60 MESH, SURFACE AREA ASSUMED AS $200 \text{ cm}^2/\text{g}$

(B) AN ADDITIONAL 95 HRS AFTER FIRST 24 HR TEST

(C) NO MEASURABLE WEIGHT LOSS DURING TESTING PERIOD

(D) POSSIBLE EXPERIMENT ERROR

TABLE 8. Leachability of Plate Glass Samples^(A)

SAMPLE	SOXHLET 72 HR		pH9				pH4	
			24 HR		168 HR		24 HR	
	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D
1 FLOAT	0.86%	7.6x10 ⁻⁴	0.05%	1.3x10 ⁻⁴	0.04%	2.9x10 ⁻⁵	0.01%	2.5x10 ⁻⁵
2 FLOAT	ND ^(C)	ND	ND	ND	0.03	2.1x10 ⁻⁵	ND	ND
6 FLOAT-LOW IRON	0.91	8.3x10 ⁻⁴	0.2	5.6x10 ⁻⁵	0.02	1.4x10 ⁻⁵	0	0
5 FLOAT	ND	ND	ND	ND	0.05	3.6x10 ⁻⁵	ND	ND
4 FLOAT	1.11	1.0x10 ⁻³	0.02	5.7x10 ⁻⁵	0.02	1.4x10 ⁻⁵	0	0
12 TWIN GROUND	0.29	3.9x10 ⁻⁴	0 ^(B)	0	0.04	2.9x10 ⁻⁵	0.01	3.7x10 ⁻⁵
7 FUSION	0.64	3.2x10 ⁻⁵	0	0	0.05	3.6x10 ⁻⁵	0.03	7.6x10 ⁻⁵

(A) SURFACE AREA RANGED FROM 2-4 cm²/g

(B) NO MEASURABLE WEIGHT LOSS DURING TESTING PERIOD

(C) ND - NOT DETERMINED

BATH SIDE

ATMOSPHERE SIDE

FIGURE 14. SEM Micrographs of Reference

Low Iron Plate Glass

ATMOSPHERE SIDE
45° TILT ANGLE

BATH SIDE
45° TILT ANGLE

FIGURE 15. SEM Micrographs of Low Iron Plate Glass Soxhlet Leached for 72 Hr

pH 4 - 24 HR

FIGURE 16. SEM Micrographs of Low Iron Plate Glass pH 4 and pH 9 Leached

FIGURE 17. Energy Dispersive X-Ray Fluorescence Analysis of Low Iron Plate Glass Sample 6

FIGURE 18. SEM Micrographs of Powdered

Low Iron Glass Soxhlet Leached for 72 Hr

Since similar behavior was not observed between the plate and crushed samples, it is suggested that experimental parameters such as surface area to volume affect the results. Hench has observed that leaching characteristics of glass are dependent upon the ratio of sample surface area to solution volume.^(4,5) As mentioned above and illustrated in Figure 18, leached surfaces of ground glass particles differ from particle to particle. Thus, it also appears that the leaching behavior of crushed particles is not consistent between similar particles. Thus, it is recommended that plate samples be used in measurements to determine the durability of proposed glass for heliostat mirrors.

SEM micrographs were obtained for the "as-received" reference and Soxhlet twin ground plate sample 12 as shown in Figure 19. The Soxhlet sample contained a few surface "holes" and some raised portions. The surface was not as greatly affected as the float sample 6. The surface texture became much more distinct by observation of the sample at a 45° tilt angle instead of 0°. This effect is demonstrated in Figure 20. The composition of the twin ground plate is similar to that of float glass as illustrated in Figure 21.

The aluminosilicate fusion glass sample 7 demonstrated no surface attack by Soxhlet leaching under SEM analysis as evidenced by the comparison of the SEM micrographs in Figure 22. As previously discussed, crushed particles of the aluminosilicate glass which had undergone Soxhlet leaching contained some surface particulate but did not contain any sponge-like texture or silica-gel layer. The composition of aluminosilicate fusion glass differs from soda-lime-silica float glass in that K and Ba are present; Ca is reduced and Al increased as illustrated in Figure 23.

In summary, the results from the Soxhlet, pH 4 and pH 9 leach tests indicate that an aluminosilicate glass has better leach resistance than soda-lime-silicates under Soxhlet and pH 9 environments. These results correlate with previous work of P. B. Adams⁽⁶⁾, illustrated in Figure 24. It is difficult, if not impossible, to predict what this implies about the desired durability of heliostat mirrors at Barstow, California. The room temperature

REFERENCE

SOXHLET - 72 HR

FIGURE 19. SEM Micrographs of Twin Ground Plate Glass Reference and Soxhlet Leached

0° TILT ANGLE

45° TILT ANGLE

FIGURE 20. SEM Micrographs of Twin Ground Plate Glass Soxhlet Leached for 72 Hr

FIGURE 21. Energy Dispersive X-Ray Fluorescence Analysis of Twin Ground Plate Glass Sample 12

REFERENCE

SOXHLET-72HR

FIGURE 22. SEM Micrographs of Fusion Plate Glass Reference and Soxhlet Leached

FIGURE 23. Energy Dispersive X-Ray Fluorescence Analysis of Fusion Plate Glass Sample 7

FIGURE 24. Glass Durability Comparison

leachability expressed as percent weight loss in acid and base conditions of all plate samples tested was between 0.01 and 0.05 wt.%, which is probably acceptable for heliostate mirrors.

Recent studies by Shelby on the effect of pH on the chemical durability of various glass plates support this observation (J. E. Shelby, Sandia Livermore, personal communication). Plate glass samples were suspended in a static solution maintained at 80°C. The results as illustrated in Figure 25 indicate that the durability of all the glasses studied are roughly similar at any pH and essentially independent of pH at $\text{pH} \leq 10$. Shelby noted that all glasses would encounter serious problems if exposed to $\text{pH} > 10$ as might be obtained if a thin layer of water was allowed to remain in contact with glass surface for an extended time. Heliostat designs which allow such conditions should be strongly discouraged.

Further studies need to be conducted to determine the kinetics of surface defects due to leaching and their effects on glass/mirror properties. Penetration or alteration layer depth should be determined versus temperature and time under leach conditions similar to the test site environment. Weight loss measurements are sufficient for scoping tests but kinetics are necessary to correlate and predict behavior in the actual environment. Specularity and transmission measurements must also be made on the leached samples to determine the effect of the leached surface on heliostat performance.

The following conclusions can be made:

- Weathering or leaching of glass heliostats may effect performance by
 - refractive index change due to surface roughness
 - refractive index change due to surface compositional variations
 - material dissolution
- Leaching models and tests are established but correlation to actual field conditions and performance is required.

Figure 25. Durability of Glass Plates at 80°C.

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GLASS DURABILITY STUDIES

Viewgraphs Presented

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GLASS DURABILITY STUDIES

UNIVERSITY OF FLORIDA:

L. L. HENCH

CORNING GLASS WORKS:

P. B. ADAMS

SANDIA LIVERMORE:

J. E. SHELBY

BATTELLE NORTHWEST:

M. A. LIND

J. M. TUSIN

LATTELLE NORTHWEST LABORATORIES -
J. M. RUSIN, M. A. LIND

- **SOXHLET LEACH TEST AT 95°C**
- **pH 4 & pH 9 LEACH TEST AT 25°C**
- **OPTICAL PROPERTIES OF WEATHERED GLASS**

SALIDA LIVERMORE - J. E. SHELBY

- **EFFECT OF pH**
- **STATIC TEST AT 80°C**
- **EDGE EFFECTS**
- **INDEPENDENT OF pH AT
 $pH \leq 10$**

CORNING GLASS WORKS - P. B. ADAMS

- **STATIC AND CYCLIC CONDITIONS**
- **HUMIDITY TEST AT 50 °C**
- **OUTDOOR EXPOSURE TESTS**

EFFECT OF SURFACE AREA & SOLUTION VOLUME

LEACHING PROFILE DETERMINATIONS

SOLUTION ANALYSIS - AA, AE

INFRARED REFLECTION SPECTROSCOPY - IRRS

SCANNING ELECTRON MICROSCOPY - SEM

AUGER ELECTRON SPECTROSCOPY - AES

PHOTOELECTRON SPECTROSCOPY - ESCA

ELECTRON MICROPROBE ANALYSIS - EMP

SUMMARY

- **WEATHERING OR LEACHING OF GLASS HELIOSTATS MAY EFFECT PERFORMANCE BY:**
 - **REFRACTIVE INDEX CHANGE DUE TO SURFACE ROUGHNESS**
 - **REFRACTIVE INDEX CHANGE DUE TO SURFACE COMPOSITIONAL VARIATIONS**
 - **MATERIAL DISSOLUTION**
- **LEACHING MODELS AND TESTS ARE ESTABLISHED BUT CORRELATION TO ACTUAL FIELD CONDITIONS AND PERFORMANCE IS REQUIRED**

FIGURE 24. Glass Durability Comparison

leachability expressed as percent weight loss, in acid and base conditions of all plate samples tested was between 0.01 and 0.05 wt%, which is probably acceptable for heliostat mirrors.

Further studies need to be conducted to determine the kinetics of surface defects due to leaching and their effects on glass/mirror properties. Penetration or alteration layer depth should be determined versus temperature and time under leach conditions similar to the test site environment. Weight loss measurements are sufficient for leaching tests, but kinetics are necessary to correlate and predict behavior in the actual environment. Specularity and transmission measurements must also be made on the leached samples to determine the effect of the leached surface on heliostat performance.

FIGURE 1. Specular Transmittance of the Hanford-D Glass

FIGURE 2. Hemispherical Transmittance of the Hanford-D Glass

FIGURE 3. Hemispherical Reflectance of Hanford-D Glass

The broad Fe^{2+} absorption band at 1100 nm has diminished in intensity in the exposed area. The magnitude of the reflectance decrease at 1100 nm is not sufficient to account for the transmission increase. It is therefore reasonable to assume that the concentration of Fe^{2+} has decreased. It has been suggested that solarization could raise the oxidation state of the iron from the 2+ to the 3+ state, thus increasing the absorption around 380 nm. It is not clear that this data supports this thesis. Further measurements are required to determine the exact mechanisms for the observed changes. It is clear, however, changes in transmittance are due to both surface and bulk effects.

LEACHABILITY OF PLATE GLASS SAMPLES(A)

SAMPLE	SOXHLET 72 HR		pH9				pH4 24 HR	
			24 HR		168 HR			
	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D	WT%	G/CM ² -D
	0.86%	7.8x10 ⁻⁴	0.05%	1.3x10 ⁻⁴	0.04%	2.9x10 ⁻⁵	0.01%	2.5x10 ⁻⁵
	ND(C)	ND	ND	ND	0.03	2.1x10 ⁻⁵	ND	ND
	0.91	8.3x10 ⁻⁴	0.2	5.6x10 ⁻⁵	0.02	1.4x10 ⁻⁵	0	0
	ND	ND	ND	ND	0.05	3.6x10 ⁻⁵	ND	ND
	1.11	1.0x20 ⁻³	0.02	6.7x10 ⁻⁵	0.02	1.4x10 ⁻⁵	0	0
	0.29	3.9x10 ⁻⁴	0(B)	0	0.04	2.9x10 ⁻⁵	0.01	3.7x10 ⁻⁵
	0.04	3.2x10 ⁻⁵	0	0	0.05	3.6x10 ⁻⁵	0.03	7.6x10 ⁻⁵

(A) SURFACE AREA RANGED FROM 2-4 CM²/G

(B) NO MEASURABLE WEIGHT LOSS DURING TESTING PERIOD

(C) ND - NOT DETERMINED

FUNDAMENTALS OF GLASS WEATHERING PROBLEMS

by

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excerpted from Glass Corrosion

OVERVIEW

Deterioration of the optical quality of glass surfaces by weathering can be a serious problem to both producers and consumers of glasses. Although archeologists may find weathering useful for determining the historical background of glass fragments, the usual objective is to understand weathering in order to prevent it. The primary emphasis of this chapter is on weathering of high durability glass compositions. Some composition-dependent results are presented that should be generally applicable to understanding and preventing deterioration of specialty and historical glasses.

The experiments described in this chapter show that the mechanism of weathering is a near-surface process and is strongly influenced by glass composition, percent relative humidity, temperature, surface treatments, geometric effects such as orientation and distance of separation of glass surfaces, and affinity of the glass surface for water. The latter (i.e., absorption and removal of water from glass surfaces) has been studied in depth by others (Adams, 1961; Huang et al, 1972). Matson (1949) has also investigated the hygroscopicity of soda-lime-silica glasses and found a correlation between the potential of glass to absorb water (hygroscopicity) in a 98% r.h. environment and durability in an aqueous solution.

TYPES OF WEATHERING

As already discussed in Chapter 1, weathering may be categorized by the extent of aqueous precipitation that accumulates on the glass surface during exposure to humid atmospheres. Type 1 weathering occurs when sufficient quantities of moisture collect on the surface to form visible droplets which eventually lead to "runoff". During Type 2 weathering a thin layer of condensation or fog forms on the glass but evaporates before visible droplets form. Type 2 weathering is encountered when glass is subjected to mild humidity-temperature changes, such as during storage or shipment, while Type 1 weathering occurs on glasses exposed to extreme climatic changes. Such cyclic conditions may be experienced by glass of exposed window panes in

northern climates.

As in aqueous corrosion, both structural as well as chemical changes occur within the surface of glass during weathering. In both forms of attack it is believed that Na^+ ions diffuse from the bulk to the surface of the glass and H^+ ions diffuse from the surface into the glass to occupy positions vacated by the Na^+ ions. In static aqueous corrosion the Na^+ ions dissolve at a rate relatively independent of the Na^+ solution concentrations for $\text{pH} \leq 9$. (Douglas and El-Shamy, 1967; El-Shamy et al, 1972). For Type 2 weathering large quantities of solution are not available to remove the Na^+ ions from the surface. Consequently, these ions must occupy sites on the glass surface until they react with CO_2 or other reactive gases present in the atmosphere to form stable salts (Simpson, 1958; Tichane, 1966).

The corrosion behavior of glass subjected to Type 1 weathering may also be affected by the physical arrangement of the glass article. Plate glass stored with the large flat surfaces parallel to the floor will have a greater tendency to retain condensed water vapor than will those with large flat surfaces perpendicular to the floor. Glasses stacked parallel to the floor are more likely to experience static corrosion in which total surface breakdown is the primary mode of corrosion while those stacked perpendicularly will be subjected to dynamic corrosion where selective alkali leaching is the principal corrosion mechanism.

The separation distance of the glass sheets stacked for storage is also an important factor in glass weathering durability. Moisture condensate between sheets of glass stacked close together may be extremely corrosive since the amount of glass exposed to the moisture is double that for the non-stacking case. This condition can lead to rapid pH changes in the condensed moisture, with subsequent deterioration of the glass surface. This situation becomes more critical as the glass separation distance decreases, due to a simultaneous increase in the glass surface area-to-solution volume ratio.

Figure 1. Compositional profiles for indise container surface, as cast.

The resistance of glass to weathering can be improved with various surface treatments. Treatment with SO_2 gas apparently results in the dealkalization of the outer and near surface of the glass. The SO_2 gas reacts with the alkali species to form a salt which may be rinsed off at the glass factory or may remain on the glass surface during weathering unless runoff occurs. This SO_2 dealkalization process results in a silica-rich layer that protects the glass against surface deterioration during weathering.

The surface of a fresh, "non-weathered" container consists of three compositional regions. The "near" surface, 0-50 Å, is rich in Na_2O and CaO . The "intermediate" surface over a range of 50-400 Å is depleted in Na_2O and CaO and rich in SiO_2 . The "far" surface region is reached at 400-900 Å with varying $\text{Na}_2\text{O}/\text{CaO}$ ratios. At a depth of approximately 900 Å the bulk glass composition is reached (see figure 1).

A large number of samples of various compositions have been analyzed by the above procedure. It has been found that an alkali-enriched layer at the outer surface is a common characteristic of soda-lime-silica glasses which have not undergone special surface treatments. This characteristic is also observed using ISS (Mishmash, 1975) and SIMS analyses (see below). In order to understand the origin of the characteristic compositional profile shown in figure 1 a series of experiments were performed.

The rate of the reaction is so rapid, even at room temperature, that the zones are established within five minutes. As shown by the Auger Spectra in figure 2. It is reasonable to expect that the reaction zones appear within seconds upon exposure of a hot glass surface to moisture upon exiting from the annealing Lehr.

To provide more direct information concerning the hydrogen ion concentration profile, analysis of an air-exposed glass surface was carried out using secondary ion mass spectroscopy (SIMS). This is a relatively new surface analysis technique which mass analyzes material sputtered off the surface in high vacuum by a 1.5 KV He/Ne ion beam. Figure 3 presents SIMS data obtained for a

Figure 2. Changes in the surface composition of soda-lime-silica glass during exposure to different environments.

Figure 3. SIMS compositional profile of an ordinary glass slide.

(Courtesy of M. J. Vasile, Bell Telephone Laboratories,
Murray Hill, N. J.) 257

Figure 4. Infrared spectra of commercial glass for
Type 2 weathering at 100°C-100 percent R.H.

Figure 5. Infrared spectra of commercial glass for
Type 2 weathering at 50°C-100 percent R.H.

Figure 6. Infrared spectra of commercial glass for Type 2 weathering at 25°C-100 percent R.H.

(a)

(b)

(c)

Figure 7. (a) SEM of Type 2 weathered commercial glass at 100°C - 100 percent R.H. for 20 days (1300x), (b) EDXA of a particle, and (c) EDXA of an area adjacent to a particle.

commercial glass (microscope slide) which was not treated in any way prior to analysis. Our previous data indicates that the characteristic sodium concentration profile produced by water vapor reaction is observed on all glass surfaces exposed to air. Hence, although this glass is not identical (i.e., in composition or treatment) to the container glass sample discussed previously, it shows the same general characteristics.

Infrared spectra for the weathered glasses are shown in figures 4-6. As a result of weathering at 100°C, the amplitude of the S stretch peak first increases and the position of the peak shifts to higher wave numbers. This corresponds to the development of a SiO₂-rich film on the glass surface.

The S stretch peak amplitude for the glass weathered for 20 days is below that for the freshly abraded sample, but the peak maximum is at a higher wave number (figure 4). The simultaneous increase in wave number and decrease in amplitude corresponds to surface roughening due to either precipitate formation or network breakdown (Clark et al, 1977). The extent of surface roughening on the 20-day specimen is approximately equivalent to that obtained by abrading the same glass to 320 grit with SiC paper.

There is very little sodium ion decoupling from the glass network evident in the spectra of figures 4 to 6. Other studies (Sanders and Hench, 1973; Clark et al, 1976) show that extensive loss of alkali ions from the glass structure greatly diminishes the intensity at ~950 wave numbers. This is not observed for all three temperatures studied, indicating that the loss of intensity at 20 days for 100°C weathering is due to formation of surface precipitates.

A scanning electron micrograph of the glass sample exposed to Type 2 weathering for 20 days at 100°C is shown in figure 7. The presence of surface precipitates is apparent in the SEM. Electron microprobe data indicated an increase in Ca intensity at the surface of the sample during weathering, and also shows relatively constant Na and Si concentrations.

As a result of the use of several surface sensitive instruments, it is now well known that the composition of a glass surface is

usually far different from that of the bulk glass. It is also known that surface composition differences can extend many micrometers into the glass. Therefore, the surface physical chemistry of a glass is determined by the composition and structure of the surface layers existing on the glass and not by the bulk glass composition. It must be recognized, however, that the surface layers formed on a glass depend upon the bulk composition, processing history, surface roughness, and environmental history including time, temperature, pH and exposure atmosphere. Special surface treatments with sulfur, chlorine or fluorine gases at elevated temperatures cause a dealkalization of the glass surface. The resulting silica-rich surface is usually more durable than the underlying bulk glass.

The various corrosion processes described above yield several different kinds of glass surfaces that may vary in composition and structure during exposure. All of the surface types obtained during corrosion and described throughout this text are summarized in figure 8. There are five types of surfaces that are characteristic of a silicate glass at any time in its history (Hench, 1977; Hench and Clark, 1978). A type I surface has undergone only a thin, 50Å, surface layer hydration. No significant surface compositional change by either dealkalization or silica network dissolution has occurred and hence the surface composition is nearly the same as the bulk composition. Vitreous silica exposed to neutral pH solutions exhibits a Type I surface.

A Type II surface possesses a silica-rich protective film due to selective alkali ion removal. Dealcalization of alkali-alkaline-earth silica glasses with low concentration of alkali results in a Type II surface. A glass with this type of surface is reasonably durable, especially in solutions of $\text{pH} < 9$.

Two layers of protective surface films are characteristics of Type III glass surfaces. Adding Al_2O_3 or CaO to a glass composition can result in dual surface layers, such as alumina-silicate or calcia-silicate species on top of a silica-rich layer. Such glasses are very durable in both acid and alkali solutions. These protective films can be produced by dealkalization, surface structural modifications,

Figure 8. Five types of glass surfaces produced during corrosion.

or precipitation from solution.

Type IV glass surfaces also have a silica-rich film but the silica concentration is insufficient to protect the glass from rapid attack from dealcalization or network dissolution. Binary sodium-silicate or potassium-silicate glasses rich in alkali form Type IV surfaces and have poor durability.

A glass that is undergoing congruent dissolution with equivalent loss of alkali and silica exhibits a Type V surface. Because of the uniform attack, the surface composition of a Type V glass is equivalent to the bulk composition. Thus, there is little difference in the surface SiO_2 compositional profile between a Type V and Type I glass. However, a glass exhibiting Type V behavior is losing considerable quantities of ions into solution. Thus, chemical analysis of the corrosion solution distinguishes the two types. Also, a heterogeneous attack of the surface often results under Type V conditions and is visible by various microscopy or infrared reflection spectroscopy techniques. Silicate glasses exposed to conditions with $\text{pH} > 9-10$ tend towards Type V behavior.

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Thermal Storage

LOW-TEMPERATURE THERMAL ENERGY STORAGE PROGRAM

Viewgraphs Presented

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LOW-TEMPERATURE THERMAL ENERGY STORAGE
(LTTES) CONSERVES PRIME ENERGY SOURCES

LTES PROGRAM THRUST AREAS

- Annual Storage Cycle — Aquifers
Earth
Ponds
- Short-Term Storage — Building Materials
Modular — Macroencapsulated
— Bulk
- Industrial Waste Heat — Existing Storage Technologies

AQUIFER STORAGE

Support Slides •Auburn University

•Texas A&M

•LBL

•TVA

Applications •JFK Airport

•Bellingham District Heating Project

•Twin Cities Project

EARTH STORAGE

George Washington University

STORAGE IN BUILDING MATERIALS

Suntek Research Associates — PCM's in Concrete

BNL — PCM's in Polymer Concrete

RFP — To be issued in 1979

MODULAR UNITS — MACROENCAPSULATED

Dow Chemical Company — PCM's and capsules for several
temperature ranges

U. of Delaware (IEC) — Glauber's salt mixture (MP 50-
55°F) in DuPont chubs

U. of Delaware — PCM's and capsule for tempera-
(Mech. Engr. Dept) tures from 100-300°C

PCM/CONTAINER SELECTION

	PCM	MP (°C)	Container
Dow	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	27	HDPE Bottle
	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$	50	R-2 Retort Film
	$\text{NH}_3\text{Br/Urea}$	76	Polypropylene Bottle
	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	89	Drawn Steel Can
U. of Del. (IEC)	Glaubers Salt Mixture	12	DuPont Chubs
U. of Del. (ME Dept.)	NaAlCl_3	159	TBD
	ZnCl_2	286	TBD
	NaOH/NaCO_3	283	TBD
	$\text{FeCl}_3/\text{NaCl}$	152	TBD

MODULAR UNITS - BULK

Clemson University	- Direct Contact-Immiscible Fluid
General Electric	- Rolling Drum Concept
Monsanto Research Corp.	- Form-Stable Polyethylene (Chemically cross-linked)
University of Dayton	- Form-Stable Polyethylene (Radiation cross-linked)
Franklin Res. Inst.	- Heat of Crystallization

INDUSTRIAL WASTE HEAT

- Food Industry — H. J. Heinz Company, Pittsburgh
- Aluminum Industry — Intalco Aluminum Plant; District
Heating of Bellingham, Washington

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MATERIALS PROBLEMS IN REVERSIBLE CHEMICAL
REACTION STORAGE SYSTEMS FOR SOLAR ENERGY

by

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MATERIALS PROBLEMS IN REVERSIBLE CHEMICAL REACTION
STORAGE SYSTEMS FOR SOLAR ENERGY

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ABSTRACT

Materials problems encountered in the development of thermochemical energy storage systems for solar energy are discussed. Concerns with catalyzed reaction systems include effects of thermal cycling on reactor materials, catalyst availability and lifetime, and undesirable side reactions. Problems have arisen in thermal decomposition systems due to poor or variable kinetics, volume expansion effects, and poor intrinsic heat transfer properties. Reactions which make use of the heat of solution suffer least from materials problems; the major concerns are with the corrosive nature of the chemicals involved (e.g., sulfuric acid, sodium hydroxide).

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ILLUSTRATIONS

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MATERIALS PROBLEMS IN REVERSIBLE CHEMICAL REACTION STORAGE SYSTEMS FOR SOLAR ENERGY

Introduction

Solar thermal energy can be stored in three forms: (1) as sensible heat, (2) as latent heat of transitions, or (3) as chemical bond energy. In the third approach (thermochemical energy storage), solar energy, would be used to drive an endothermic reaction; the energy would be withdrawn from storage by reversing the reaction to the exothermic mode.

Compared to sensible and latent heat systems, thermochemical systems have several unique characteristics:

High Energy Densities - Thermochemical storage systems have storage densities (based on either mass or volume) ranging from about a factor of two to more than an order of magnitude greater than is possible with sensible and latent heat systems.

Ambient Storage - Energy storage at ambient temperatures is possible for thermochemical systems, i. e., chemical reactants and products can be cooled to and stored at ambient temperatures. The ability to store at ambient temperatures and still discharge at high temperatures has obvious advantages: chemical interactions between the media and storage container materials are avoided, insulation requirements are eliminated, overall system heat losses are reduced, and potential environmental impact problems (e. g., those resulting from storing copious quantities of hot material) are avoided. On the other hand, there is a penalty associated with the storage at ambient temperatures; sensible and possibly latent heats are rejected upon cooling the products to ambient. However, this reject heat may not necessarily be lost, as it may be possible to recover it elsewhere in the chemical cycle.

Long-Term Storage - In ambient storage, long-term storage with little or no degradation is possible, thus making seasonal or extended storage applications feasible.

Transportability - Chemical reactions can be selected so that the products and reactants are easily transportable, e. g., as gases in a pipeline. Therefore, the endothermic and exothermic reactors can be physically separated by long distances, and one has in effect a means of distributing solar thermal energy.

Heat Pump Capability - A heat pump can be created by combining an endothermic and exothermic reaction. It is possible, therefore, to devise a system whereby solar energy can be used to charge a storage system which provides both space heating and cooling.

Low Energy-Related Costs - The cost of an energy storage system can generally be divided into two categories: power costs and energy costs. The power-related costs are those associated with reactors, heat exchangers, etc., whereas energy-related costs are associated with raw materials, storage tanks, etc., and are generally low for thermochemical systems.

Potentially useful reactions can be categorized into (1) catalyzed reactions, (2) thermal decomposition reactions, and (3) solution/dissolution reactions. Candidate reactions in each of these categories are given in Figure 1. Major materials problems encountered during the development of energy storage systems based on these reactions are discussed below.

CATALYZED:	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$
	$2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$
	$\text{C}_6\text{H}_{12} = \text{C}_6\text{H}_6 + 3\text{H}_2$
THERMAL DECOMPOSITION:	$\text{MCO}_3 = \text{MO} + \text{CO}_2$
	$\text{MSO}_4 = \text{MO} + \text{SO}_3$
	$\text{MH}_2 = \text{M} + \text{H}_2$
	$\text{MX} \cdot \gamma\text{H}_2\text{O} = \text{MX} + \gamma\text{H}_2\text{O}$
	$\text{MX} \cdot \gamma\text{NH}_3 = \text{MX} + \gamma\text{NH}_3$
	$\text{MX} \cdot \gamma\text{CH}_3\text{OH} = \text{MX} + \gamma\text{CH}_3\text{OH}$
SOLN./DISSOLN.:	$\text{M}(\text{OH})_2 = \text{MO} + \text{H}_2\text{O}$
	$\text{H}_2\text{SO}_4(\text{DILUTE}) = \text{H}_2\text{SO}_4(\text{CONC}) + \text{H}_2\text{O}$
	$\text{NaOH}(\text{DILUTE}) = \text{NaOH}(\text{CONC}) + \text{H}_2\text{O}$

Figure 1. Candidate Reactions

Catalyzed Reaction Systems

The three catalyzed reactions which appear to be the most promising are

Simplified schematics of energy storage or transport systems based on each are shown in Figures 2 through 4. The parts of each storage system where there are major materials concerns are indicated on the figures.

Figure 2. Thermochemical Energy Storage Concept Based on the Reaction $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$

Figure 3. Chemical Heat Pipe System Based on the Reaction
 $\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$

Figure 4. Chemical Heat Pipe System Based on the Reaction
 $\text{C}_6\text{H}_{12} = \text{C}_6\text{H}_6 + 3\text{H}_2$

Effects of Thermal Cycling

Catalytic reactors are normally designed to operate under constant conditions (temperature, input, and output). However, solar energy is cyclic in nature, and the effects of thermal cycling on catalyst lifetime, reactor performance, and structural materials are unknown.

Catalyst Availability and Lifetime

The availability of an inexpensive catalyst for the endothermic reaction $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$ is a major concern. Inexpensive V_2O_5 -based catalysts have been developed for the lower temperature exothermic reaction of $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$; however, the endothermic reaction takes place at temperatures exceeding the melting point of V_2O_5 . Platinum based catalysts are effective, but they are prohibitively expensive. Transition metal oxides other than V_2O_5 are possible candidates; their effectiveness in catalyzing the decomposition of SO_3 requires verification.

Nickel-based catalysts are known to effectively catalyze the methanation/reformation reaction; thus, no catalyst development work is required for the reaction $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$. However, continued research to develop a chemical mechanistic understanding would be useful in predicting catalyst lifetime and long-term performance.

Catalysts have been developed for numerous hydrogenation/dehydrogenation reactions of the type $\text{C}_6\text{H}_{12} = \text{C}_6\text{H}_6 + 3\text{H}_2$ for use in the petroleum industry. However, the emphasis has been on "once through" reactors where 99 percent specificity is sufficient. In an energy storage application where closed cyclic operation is required, the formation of 1 percent nonreversible products on each cycle is unacceptable. Therefore, catalysts capable of at least 99.9 percent specificity for the hydrogenation/dehydrogenation reaction of interest must be developed and their performance verified.

Undesirable Side Reactions

Hydrogenation/dehydrogenation reactions suffer in that undesirable side reactions are possible; the differences in the thermodynamic stability of those related compounds that are potential products of reaction are generally not large enough to preclude the formation of undesirable products. The extent to which one product can be formed depends primarily on catalyst specificity. On the other hand, the SO_3 and CH_4 reactions are simple and straightforward chemically, and no side reactions with either are anticipated.

Corrosion

Corrosion and compatibility problems do not appear to be of major concern for the CH_4 and C_6H_{12} reactions; however, the conditions in the SO_3 system are very aggressive, and the availability of construction materials is a key question. It is unknown whether commercially available alloys can withstand the high temperature, high pressure, and simultaneous sulfidizing and oxidizing conditions. Alloy screening studies must be performed, and if necessary, an alloy development program must be initiated.

Thermal Decomposition Systems

Materials problems encountered in thermal decomposition reaction systems are generally common to all regardless of the specific reaction. Therefore, rather than discuss each reaction given in Figure 1, materials concerns associated with the general reaction

are discussed. These problems can be classified into the following areas:

- Reaction kinetic concerns
- Volume expansion effects
- Heat transfer problems

Reaction Kinetic Concerns

In general there is a lack of applicable data. Previous studies have tended to concentrate on the decomposition (endothermic) reaction; very few studies have ever been performed on the recombination (exothermic) reaction. Furthermore, almost all studies have been carried out at pressures and temperatures different from those anticipated in actual energy storage systems.

The effects of reaction cycling on reaction kinetics have not been studied to any extent. There is evidence to suggest the reaction rates will continually decrease upon cycling. Figure 5 shows data for the reaction $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$. As shown, there is a decrease in the reaction rate as the reaction is cycled; this effect has been attributed to the loss of reactive surface area due to sintering processes. However, some investigators have reported the opposite effect: rates of reaction for other reactions

Figure 5. Effect of Reaction Cycling on the Reaction Between CaO and CO₂

have been observed to hold essentially constant upon cycling. It may be that the effect of cycling is coupled to other parameters such as temperature, pressure, or the nature of the reactants/products. This area has not been explored in any detail, and there is clearly a need for materials research.

Volume Expansion Effects

Significant volume changes upon reaction can be predicted. The expansions for several reactions have been calculated based upon theoretical densities and are given in Figure 6. It is seen that volume changes of 100-200 percent upon the exothermic reaction are not unreasonable.

<u>REACTION</u>	<u>% EXPANSION</u>
$\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$	101
$\text{CaCl}_2 + 8\text{NH}_3 \rightarrow \text{CaCl}_2 \cdot 8\text{NH}_3$	195
$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$	95
$\text{MgCl}_2 + 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	230
$\text{ZnO} + \text{SO}_3 \rightarrow \text{ZnSO}_4$	214

Figure 6. Volume Changes for Some Thermal Decomposition Reactions

The possible consequences of such large changes in volume are:

- sintering
- material movement
- stress on structural materials and components
- stress on heat transfer structures

Observations made by several investigators provide some interesting examples of these consequences. Observations made by Podlasak (Martin Marietta, Denver, Colorado) during ammoniation experiments are given in Figure 7. Attempts to ammoniate CaCl_2 in a cylindrical crucible resulted in the formation of a dense plug of $\text{CaCl}_2 \cdot 8\text{NH}_3$, which then served as an impermeable barrier to the NH_3 . Complete ammoniation of the CaCl_2 was not possible. Observations made by Springer, et al (Atomics International) during their studies of the reaction $\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2$ are illustrated in Figure 8.

Figure 7. Ammoniating CaCl_2 Can Result in a Dense Inert $\text{CaCl}_2 \cdot 8\text{NH}_3$ Slug

Figure 8. Volume Expansion Effects During the Reaction $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$

Their experimental reactor, shown on the left, consisted of a closed end tube into which a cylindrical, fine mesh, stainless steel screen was welded. Calcium oxide was placed in the annulus, and water vapor was introduced from the center. Post-test examination of the reactor after numerous cycles showed:

- the screen was crushed and severely deformed
- stresses on the screen were sufficient to cause rupture at the weld
- material was not uniformly distributed
- the Ca(OH)_2 was not homogenous; hard lumps were found dispersed in loose powder

One might argue that the volume expansion effects just discussed are not materials problems, but are design and engineering problems; volume changes will undoubtedly occur upon cycling and one must design the system hardware to accommodate such changes. However, it has been observed by other investigators that volume changes with some systems are negligible; after the first exothermic cycle a bed volume is achieved which remains essentially constant for all subsequent cycles. Therefore, the materials problem of current concern is not how to handle the expansion; rather, it is to understand and predict the expansion behavior of cyclic decomposition/recombination reactions.

Heat Transfer Problems

Perhaps the most critical problem with regard to actually implementing an energy storage system based on thermal decomposition reactions is heat transfer. It is uncertain that one can efficiently and controllably deposit and extract thermal energy from a reacting solid bed. Two factors lead to inherently low heat transfer rates: (1) the solid bed is porous, and (2) the intrinsic conductivity of the chemicals is generally low. The use of an inert liquid to suspend reacting solid particles would eliminate the heat transfer problem at the expense of introducing a new set of problems including solid-liquid compatibility, particle settling, and undesirable reactions. In order to predict long-term performance and guide the heat exchanger/reactor design efforts, an in-depth understanding of the heat transfer process is required. However, any attempts to analytically model the heat transfer process will be exceedingly complex, since the bed will be undergoing continual physical and chemical changes with time.

Solution/Dissolution Reactions

Reactions which make use of the heat of solution appear to suffer least from materials problems. An example of such a reaction is one we can all identify with, namely

A simplified schematic for the reaction is shown in Figure 9. The heat transfer problem which plagues thermal decomposition reaction systems is of no consequence here; heat transfer is facilitated by the fact that we have a liquid system. The reaction is simple and straightforward; side reactions and uncharacterized kinetics are not problems. Acid carryover during the energy charge step is a potential problem, which can be circumvented by appropriate component design. The only problem of major concern is corrosion. However, this problem can be circumvented by selecting the appropriate temperature range of operation.

Figure 9. Energy Storage System Based on the Heat of Solution of Sulfuric Acid

Other Materials Problems

Several materials problems exist which have not been discussed yet:

- alternate reactions
- gas storage materials
- corrosion

The reactions discussed above have been singled out as having potential, and efforts are being made to develop energy storage systems based on them. However, they did not evolve from a complete and comprehensive screening procedure in which all possible reactions were evaluated. Quite probably there are other reactions which merit consideration. There will continue to be a need for new and innovative ideas and alternate reactions.

Many decomposition reactions involve the generation of noncondensable gases such as O_2 and CO_2 that must be compressed and stored at high pressures. A severe cost penalty is associated with gas compression and storage. Materials which can serve as a solid-state, low-pressure storage medium for hydrogen are known to exist. Materials serving a similar function for O_2 and CO_2 would have a significant impact on the system economics of thermal decomposition storage systems.

While corrosion has been discussed for several specific reactions, its importance cannot be overemphasized. All systems are bothered by potential corrosion problems. We are not only concerned with effects at high temperatures; many of the low-temperature reactions involve chemicals which are notoriously bad from the standpoint of corrosion (e. g., $MgCl_2$, $CaCl_2$).

Summary

The major materials problems being encountered during the development of thermochemical storage and transport systems have been discussed. It is not possible to describe in detail all of the materials problems being addressed or anticipated; rather, an attempt was made to highlight the most significant problems we are currently aware of. While many problems exist, none seem to be insurmountable, and reversible chemical reactions will no doubt play a role in the successful development and use of solar energy.

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HIGH TEMPERATURE THERMAL
ENERGY STORAGE PROJECT

Viewgraphs Prepared*

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*Prepared for, but not presented at this workshop.

LEWIS RESEARCH CENTER

HIGH TEMPERATURE THERMAL ENERGY STORAGE PROJECT

OBJECTIVE: DEVELOP AND DEMONSTRATE TECHNOLOGY FOR COST AND PERFORMANCE
EFFECTIVE THERMAL ENERGY STORAGE FOR END-USE APPLICATIONS

SOLAR THERMAL POWER SYSTEM APPLICATIONS

DIURNAL STORAGE

- LARGE STEAM RANKINE POWER CYCLES USING WATER/STEAM RECEIVERS
- LARGE STEAM RANKINE POWER CYCLES USING MOLTEN SALT/LIQUID METAL RECEIVERS
- LARGE BRAYTON POWER CYCLES
- SMALL RANKINE POWER CYCLES

BUFFERING STORAGE

- LARGE STEAM RANKINE POWER CYCLES
- SMALL DISH MOUNTED HEAT ENGINES

LONG DURATION STORAGE APPLICATIONS

ADVANCED TECHNOLOGIES

- TRANSPORT
- VERY HIGH TEMPERATURE STORAGE
- SUPPORTING RESEARCH AND TECHNOLOGY

TOTAL ENERGY SYSTEMS

HIGH TEMPERATURE THERMAL ENERGY STORAGE

MEDIA

SENSIBLE HEAT

LATENT HEAT

LIQUIDS

- o HIGH TEMPERATURE WATER
- o ORGANIC COMPOUNDS
(OILS, SILICONES)
- o INORGANIC COMPOUNDS
(SALTS, SULFUR, METALS)

SOLIDS

- o METALS
(IRON/STEEL)
- o MINERALS
(SILICATE, GRANITE)
- o CERAMICS
(ALUMINA, MAGNESIA)

SOLID/LIQUID

- o NITRATES
- o NITRITES
- o HYDROXIDES
- o CHLORIDES
- o CARBONATES
- o FLUORIDES
- o FUSIBLE METAL ALLOYS

SOLID/SOLID

- o SODIUM SULPHATE
- o SODIUM HYDROXIDE

MATERIALS CONSIDERATIONS - GENERAL

MEDIA

CONTAINMENT

- o THERMAL PROPERTIES
- o CORROSION DATA
- o PHYSICAL PROPERTIES
- o CORROSION MECHANISMS
- o CONDUCTIVITY ENHANCEMENT
- o LIFE
- o STABILITY
- o COSTS
- o SAFETY
- o AVAILABILITY

THERMOPHYSICAL AND CHEMICAL CHARACTERISTICS ARE ESSENTIAL TO MAKING
PERFORMANCE ESTIMATES AND MATERIAL RESPONSE PREDICTIONS

SENSIBLE HEAT STORAGE MATERIALS CONSIDERATIONS

FLUIDS: (ORGANIC)

SAFETY

STABILITY

COMPATIBILITY

DEGRADATION

LIQUID METALS:

REACTIVITY

CONTAINMENT CORROSION

SAFETY

MOLTEN SALTS:

DECOMPOSITION/OXIDATION

STABILITY

COMPATIBILITY

CONTAINMENT CORROSION

INORGANIC SOLIDS:

PACKED BED FLUID COMPATIBILITY AND STABILITY

THERMAL PROPERTIES OF SOLIDS AT HIGH TEMPERATURES

CORROSION CHARACTERISTICS

LATENT HEAT STORAGE MATERIALS CONSIDERATIONS

- o HEAT CAPACITY MEASUREMENTS
- o HEAT OF FUSION
- o THERMAL CONDUCTIVITY
- o NON-EQUILIBRIUM EFFECTS
 - KINETICS OF PHASE TRANSFORMATION
 - SUPERHEATING/COOLING
 - SELF DECOMPOSITION DUE TO THERMAL CYCLING
- o LONG TERM EFFECTS OF IMPURITIES
- o MAINTENANCE OF MOLTEN EUTECTIC SALT COMPOSITION
- o VOLUMETRIC CHANGES
- o VAPOR PRESSURE
- o TRANSPORT PROPERTIES
 - WETTING CHARACTERISTICS
 - VISCOSITY
 - DENSITY VARIATIONS

ADVANCED THERMAL ENERGY STORAGE CONSIDERATIONS

650°F (350°C)

SENSIBLE UTILIZATION TEMPERATURE RANGE

650°F TO 2000°F

LATENT UTILIZATION TEMPERATURE RANGE

650°F TO 1500°F

CONTAINMENT MATERIALS

PRESTRESSED CAST IRON

PRESTRESSED CONCRETE

MILD STEELS

COPPER AND NICKEL ALLOYS

} UP TO 1000°F

STAINLESS STEELS

NICKEL-CHROMIUM ALLOYS

} UP TO 2000°F

ADVANCED HIGH TEMPERATURE TES
NASA-LEWIS MATERIAL RELATED CONTRACTS

DESIGN AND FABRICATE SODIUM SULFATE PEBBLE BED (CALMAC)
LABORATORY STUDY SODIUM HYDROXIDE SYSTEM (C&W)
FABRICATE NRL ENERGY STORAGE BOILER TANK (NRL)
LABORATORY STUDY OF CARBONATE SYSTEMS (IGT)
ASSESS METAL FLUORIDES (PENNWALT)

PROPERTY MEASUREMENTS OF METAL ALLOY MEDIA (UNIVERSITY OF DELAWARE)
HEAT TRANSFER ASPECTS OF MOLTEN SALT SYSTEMS (ENERGY FOUNDATION OF TEXAS)
ASSESS LATENT HEAT MEDIA (IGT)

ADVANCED HIGH TEMPERATURE TES

SUMMARY - MATERIAL CONSIDERATIONS

EVALUATE CANDIDATE MEDIA

DETERMINE PROPERTIES

DETERMINE CORROSION EFFECTS

DETERMINE STABILITY OF MEDIA

CONDUCT SYSTEM ANALYSIS FOR ECONOMIC EFFECT

COMPATIBILITY PROBLEMS ASSOCIATED WITH
SENSIBLE HEAT STORAGE SYSTEMS

Viewgraphs Presented

by

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PROBLEMS

- IN PHASE CHANGE SYSTEMS -
- IN THERMOCHEMICAL SYSTEMS -
- IN SENSIBLE HEAT SYSTEMS -
 - THERMAL COMPATIBILITY
 - MATERIALS COMPATIBILITY
- REPRESENTATIVE TESTING

THERMAL COMPATIBILITY

- HYDROCARBON FLUIDS: 300°C - 360°C
- SILICONE FLUIDS: 360°C - 400°C
- MOLTEN SALTS: 400°C - ?
- GRANITE ROCK: THERMAL CYCLING
220°C - 300°C
300°C - 550°C

Fig. 1a - Schematic Diagram of a Typical Thermal Storage Unit

Fig. 1b - Schematic Diagram of Test Vessels Used by Rocketdyne

Fig. 1c - Schematic Representation of Test Vessels Used in Published Reports

Fig. 2 - Schematic Diagram and Picture of Test Vessels Used in Sandia Studies

MATERIALS COMPATIBILITY

- HYDROCARBON OILS WITH ROCK, SAND & METAL
- SILICONE FLUIDS WITH ROCK, IRON ORE & METAL
- NITRATE (NITRITE) MOLTEN SALTS WITH ROCK & IRON ORE

CONCLUSIONS

- THERMAL COMPATIBILITY MUST BE DETERMINED WHEN OPERATING NEAR TEMPERATURE LIMITS
- VESSEL DESIGN MUST BE REPRESENTATIVE OF ACTUAL USE CONDITIONS
- THERE MAY NOT BE A SUITABLE "UNIVERSAL" TEST VESSEL
- ECONOMIC EVALUATION IS NOT CONTINGENT UPON KNOWLEDGE OF THE BREAKDOWN MECHANISM

Dup

CORROSION IN MOLTEN SALTS USED FOR SOLAR
THERMAL STORAGE APPLICATIONS *

by

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Introduction

Molten salts which are to be used for thermal storage should have low viscosity, high thermal conductivity, and should be chemically stable. The first two properties are required for optimization of heat transfer characteristics. The third insures long life for the heat transfer fluid, and this is especially important for low cost solar applications. The design and operating characteristics of the thermal storage system will determine the set of design parameters which will be important in the selection of particular molten salt system. Of these parameters, the following are the most critical: 1) operating temperature, 2) operating pressure, and 3) materials compatibility. An additional characteristic of a solar system which is important is the cyclic nature of operation. The cyclic temperature and pressure will cause materials problems which may be unique to solar thermal storage systems and this will be discussed further below.

Several reviews, surveys, and handbooks are available for properties of molten salts.⁽¹⁻⁴⁾ Two of these⁽³⁻⁴⁾ deal specifically with thermal storage applications, but primarily for service above 500°C. In addition, these latter two references discuss materials compatibility in molten salts with the emphasis on high temperature systems. Shimotake, et. al.⁽⁵⁾ have reviewed molten salt corrosion problems, with the principle interest being molten halides for battery applications. Koger⁽⁶⁾ has reviewed the large body of data which is available for materials compatibility in molten fluorides. Other individual systems have also received some attention in the scientific literature,^(7,8,9,10) but the data is not broad and usually does not cover

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a wide range of operating conditions nor a variety of materials. A comprehensive review of the literature on molten salt corrosion will not be given here, but some of the broad outlines of corrosion behavior will be discussed below, some of which is presented in these references. This will serve as a guide for materials problems which may be anticipated. In addition, the compatibility of materials with a specific molten salt system will be discussed at some length. This system is the molten nitrate - nitrite class of salts which have been selected for solar thermal storage applications. The paper will be concluded with a brief summary of recommendations for areas of future work on the molten nitrate - nitrite salts to increase the reliability of materials behavior in solar systems.

Corrosion in Molten Salts

Corrosion behavior in molten salts will be determined by either thermodynamics or kinetics, or a combination of both. Thermodynamic stability of a metal-molten salt combination guarantees that kinetics are not important. This may be achieved for a rather restricted number of systems, especially for the more important structural metals or alloys. The molten alkali halides offer the widest range of stability for the largest number of metals, i.e., there is no spontaneous reaction between the melt and the metal, but their high melting points restrict their applicability somewhat. The lower melting molten salts such as the alkali metal nitrates have very limited compatibility on a thermodynamic basis, but may be, and are, widely used because metals corrode only very slowly over a wide temperature range.

Johnson,⁽¹¹⁾ and others^(1,4,7) have given three general thermodynamic properties which determine the corrosion behavior of a metal in a molten

... ..

- 1) the nobility of the metal
- 2) the stability of the melt, and
- 3) the redox potential of the melt.

The first two relate the relative stability of the pure melt and the metal or alloy, and the third includes the effect of dissolved impurities such as water or oxygen. Such impurities would be cathodically active, and could increase the anodic dissolution rate of the metal. These properties would be most important for systems in which the metal has no passivity. The halide molten salts are specific examples of such systems in which the natural metal oxides are not passive and offer no protection. Careful removal of impurities, and equilibration of the molten salt with a very active metal, are necessary to reduce the corrosion of normal structural metals and alloys to negligible values in many of the alkali halide melts. Such techniques have been adopted for the widely used system LiCl-KCl eutectic,⁽¹²⁾ and for molten fluorides.⁽⁶⁾

Koger⁽⁶⁾ has reviewed the materials problems that may be alleviated in molten fluorides by careful attention to maintaining thermodynamic stability. Selective dissolution of the most active component in an alloy (usually Cr) with subsequent void formation was solved for the molten fluorides by maintaining the redox potential more negative (active) than the active component. Mass transfer of the metal from hot to cold parts is also observed in fluorides, but can be minimized by controlling the redox potential of the melt as described above. This mass transfer was found to be negligible for this system by alloy selection.

These few examples serve to illustrate the type of problems encountered in many molten salt systems, but are not a complete survey. From a design point of view, they represent the kind of behavior that may be expected in

molten halides, or other systems in which there are no protective films. There are even a small number of halide systems in which a protective, non-soluble, metal halide film is formed. One of these systems is the equimolar NaCl-AlCl₃ system, in which many of the transition metal dihalides are insoluble⁽¹³⁾ and the metals have quite stable passive behavior. Increasing the concentration of AlCl₃, however, renders the halides soluble and this destroys the passivity. In general, the molten halides require that stability of container metals be maintained in a thermodynamic sense, and this suggests that rigorous attention must be paid to maintaining high purity systems.

The oxyanion molten salts, of which the nitrates are an example, would be expected to attack most metals and the thermodynamic principles outlined above cannot be used to establish compatibility. If these molten salts are to be used, one must then depend on kinetic stability. Kinetic stability is found in systems where there are protective films on the metal or alloy, and this is usually an oxide. In molten nitrates any stability of metals is almost completely kinetic because of the oxidizing ability of the nitrates. Because these salts have been chosen for solar thermal storage studies, some further discussion of their properties will be given. This will illustrate the kinds of problems which may be encountered in other oxyanion systems as well.

The thermodynamic properties of metals in nitrate salts will be useful because of the guidance that is provided for enhancing the thermodynamic stability of the system, although the primary stability is kinetic in nature. This data has been summarized for several systems^(14,15) in the form of electrode potential vs oxide ion activity (i.e., pO^{2-}) diagrams. The oxide ion is chosen because it is the primary base for the system in the Lux-Flood sense. However, recent evidence has been summarized by Flambach⁽¹⁶⁾

which indicates the importance of peroxide (O_2^{2-}) and superoxide (O_2^-) ions as well. An earlier review⁽¹⁷⁾, suggested that these ions may be dominant in concentration over the oxide ion, except at extremely large concentrations of oxide ion. The oxide ion may be derived from self ionization reactions such as

or from decomposition reactions of the nitrate, e.g.,

but more especially from the nitrite

These decomposition reactions become more important at high temperatures.

Reactions of the oxide ion with the melt may yield the peroxide and superoxide ion, in the following way

and

If the melt is saturated with oxygen, the following will be important as well

Thermodynamic data have been summarized in the form of potential vs pO_2^{2-} and pO_2^- diagrams to reflect this chemistry, but the choice of one over the other may be somewhat arbitrary. In general, the larger the value of pO_2^{2-} (or pO_2^- or pO_2^-) the greater the range of stability of the metal. If the metal forms a passivating oxide however, the kinetic stability would be favored

by a low value of pO^{2-} (high O^{2-} concentration). A limit would be reached at high concentration of O^{2-} if an oxyanion like ferrate or aluminate is found.

The stabilities of nitrates and nitrites have been measured with respect to thermal decomposition as well. Both kinetic and equilibrium measurements have been made. The nitrates decompose at low temperatures^(18,19) according to

At 300°C, the equilibrium concentration of nitrite was found to be 2×10^{-4} molal at 0.85 atmospheres O_2 in $NaNO_3/KNO_3$. Nitrites decompose according to

where the oxide ion has been used to designate the basic species in solution, although other species are expected as discussed above. These results suggest that one should use air or O_2 as an ambient gas in nitrate (or nitrite) systems in order to minimize decomposition, and fix the oxide species concentrations as well.

Acid-base reactions which may influence the corrosion kinetics involve changes in the concentration of the oxide ion (or its derivatives). Such reactions are:

1. Reaction of the melt with ambient carbon dioxide.

The solubility of carbonate has been measured in $NaNO_3/KNO_3$ as a function of temperature,⁽²⁰⁾ and several other nitrates and nitrites as well.⁽²¹⁾ The solubility of Na_2CO_3 in equimolar $NaNO_3/KNO_3$ was found to be 0.025 molal at 530°K, or extrapolated to be 0.575 molal at 823°K.

2. Reaction of metal oxides with excess oxide.

The soluble product might be ferrate, for example, and this would increase the corrosion rate.

3. Reaction with silica.

This reaction would restrict the use of silica in molten salts. Soluble silicates could also influence corrosion of metals because of the subsequent formation of insoluble siliceous compounds.

4. Oxide buffer reactions. An oxide buffer reaction is illustrated by the equilibrium

and this fixes the O^{2-} concentration in the melt. The use of a $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ as an oxide buffer for molten salts would be useful for controlling the concentration of carbonate by the reaction

Such buffers could be useful in modifying corrosion rates directly as well. (22)

The redox chemistry of the nitrate melts strongly influence corrosion rates and reflect the oxidizing properties of the melt. In addition to the nitrate and nitrite ions, the peroxide and superoxide ions are strong oxidizing agents and may be the primary oxidizing species in such melts. Several reactions are observed in molten nitrates which do not proceed in aqueous nitrate solutions to any extent. Cr(III) for example is not stable in nitrates but is oxidized according to, (23)

or

The chromate/dichromate system is a strong oxidizing system in addition to

having interesting acid-base chemistry, and can accomplish the oxidation of nitrite according to

This reaction suggests that nitrate melts could be stabilized with respect to thermal decomposition by addition of the $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ buffer in air or oxygen.

Specific corrosion results on several iron alloys in molten $\text{NaNO}_3\text{-KNO}_3$ and $\text{NaNO}_3\text{-KNO}_3\text{-NaNO}_2$ have been measured recently. ^(24,25) A summary of these data are:

1. oxide formation is somewhat faster in the nitrite system than in air,
2. 310 and 316 SS have excellent corrosion resistance,
3. carbon steel and low-Cr steels oxidize about 100 times faster than the stainless steels,
4. scaling of carbon steel may not be protective, and
5. cathodic protection of stainless steels (i.e. chromium) should not be attempted (see also (11)).

Result 4 would be important for cyclic systems especially where a loosely adherent layer may be detached with alternate expansion and contraction caused by temperature variations.

Summary and Recommendations

This brief review has been directed at: 1) identification of corrosion problems that have been observed in molten salts, and 2) classification of properties of the melts that have been identified as important in determining corrosion behavior. In addition, specific discussion of nitrate molten salts was given as a class of systems in which corrosion behavior is dominated by kinetics. Several recommendations are appropriate for future work on the experimental work reported. ^(24,25) Solar thermal storage requirements are for long life and much more work has to be done before a materials selection is made even for pilot plant operations. The specific areas of work which should be pursued are:

1. Stability diagrams for iron, nickel, and chromium in nitrates should be constructed. This will serve to focus attention on acid-base properties which should be controlled for optimum performance. Some work on the iron system has been done. (14)
2. The effect of ambient gases should be studied. This will influence the stability of the melt, and O_2 seems to be the best choice at present. N_2 is not in equilibrium with the nitrate melts at low temperatures ($\sim 500^\circ C$) and should not be used. It will act as an inert gas, and in a flowing system may accelerate melt decomposition.
3. More complete investigation of acid-base behavior and of oxide buffers would be very useful. The inclusion of $CrO_4^{2-}/Cr_2O_7^{2-}$ is especially promising.
4. Development of an oxide sensitive electrode would be of use for the acid-base studies above, and might have use as a monitoring sensor for a storage system.
5. Development of a carbonate sensitive electrode would be useful for a system which is open to the air. This could be used for monitoring as well. Use of an oxide buffer such as $CrO_4^{2-}/Cr_2O_7^{2-}$ might make this unnecessary.

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CORROSION IN MOLTEN SALTS USED FOR SOLAR
THERMAL STORAGE APPLICATIONS*

Viewgraphs Presented

by

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CHEMISTRY OF THE MOLTEN NITRATES

DECOMPOSITION

$$K_{550^\circ\text{C}}(\text{KNO}_3) \sim 10^{-2}$$

OXIDE AND OXIDE-RELATED SPECIES

ACID-BASE PROPERTIES

REDOX REACTIONS

Scheme of the different regions established in the potential/ pO_2 diagram
(S. L. Marciano and A. J. Arvia, 1974)

Nitrate Systems for Thermal Storage

Kinetically stable, but Limited

Thermodynamic Stability

Excellent Oxidizing Properties

Specific Chemistry to Control Corrosion

Oxide concentration

Ambient gases

Oxyanion Molten Salts

Low Melting Points

Good Physical Properties

- * Good thermal conductivity
- * Low viscosity
- * Stable at low temperatures

Examples

Nitrates

Carbonates

Sulphates

(chlorates, acetates, phosphates)

Halide Environments

Oxides are non-protective

Redox potential of melt is important relative to equilibrium potential of metal

Ways to maintain compatibility

Add an active metal as getter

Cathodically protect structural metal

Problems

Mass transfer

Selective attack (void formation)

Pumping a Highly Conductive Electrolyte in
a Magnetic Field

Stress corrosion cracking

Factors Which Determine Corrosion Properties

Relative Thermodynamic Stability of Melt and Metal

- * Stability of the molten salt
- * Nobility of the metal

Redox Potential of the Melt

Film Forming Reactions

Oxide
Chloride
Fluoride

Systems for use under 500°C

Oxyanion Molten Salts

Halide Molten Salts (AlCl_3 containing)

Salt Hydrates ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)

Materials Compatibility in Thermal Storage

System Requirements

Cyclic Temperature

Low Pressure

Long Life

Selection Factors

Temperature less than 500°C

Properties of individual molten
salt systems

Thermodynamic stability

Kinetic stability

Types of problems encountered or
anticipated

Equilibrium concentrations of several ions in a nitrate melt.

Figure 1. Processes Which Control Cracking of Ti-8Al-1Mo-1V in Molten LiCl-KCl.

TO BE DONE:

- o CHROMIUM, NICKEL, IRON CHEMISTRY IN
MOLTEN NITRATES AS A FUNCTION OF
OXIDE ION CONCENTRATION
- o CHEMISTRY OF NITRATES AND CHOICE OF
AMBIENT GAS (USE O_2)
- o STABILITY DIAGRAMS CONSTRUCTED TO
SUMMARIZE THERMODYNAMIC PROPERTIES
- o OXIDE SENSITIVE ELECTRODE
- o CARBONATE SENSITIVE ELECTRODE

SUMMARY OF CORROSION DATA

- OXIDE FORMATION SOMEWHAT FASTER IN MOLTEN NITRATES THAN AIR
- 310 AND 316 SS HAVE EXCELLENT CORROSION RESISTANCE
- CARBON STEEL AND LOW -CR STEELS OXIDIZE ABOUT 100X FASTER THAN SS

*DO NOT CATHODICALLY PROTECT STAINLESS STEELS
(OR CHROMIUM)

* $\text{CrO}_4^{-2}/\text{Cr}_2\text{O}_3^{-2}$ REDUCE OXIDATION RATE

*SCALING OF CARBON STEELS MAY NOT BE PROTECTIVE

*GAS PHASE MAY BE IMPORTANT (USE O_2)

HIGH TEMPERATURE THERMAL ENERGY STORAGE

MATERIALS AND THEIR PROPERTIES

by

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It is apparent that large-scale energy storage will become important in meeting our national energy needs. Large energy storage systems not only increase the efficiency of the existing electric power grids through load leveling, but are required in the exploitation of intermittent energy sources such as solar-electric power. Therefore, it is important to develop the technology for efficient storage of energy economically.

The thermal energy storage systems are particularly attractive for the storage of solar energy where heat is the form of energy produced or demanded. The conservation benefits can come largely from energy storage subsystems. Thermal energy can be stored either through the latent heat or through the sensible heat. In sensible heat storage, the temperature of the storage material is raised or lowered during charge or discharge, respectively. Because water has a specific heat of $1 \text{ cal/}^{\circ}\text{C gm}$, for a temperature change of 30°C , the energy that can be stored is 30 cal/gm . Though stored energy can be increased by increasing the volume and temperature, the costs of insulation and large containers needed make it less desirable. The storage using rock bins uses forced air and therefore needs more collector area. The system requires a large volume and there are problems of dust buildup in the bins and possible bacterial and fungal infestation, particularly in humid climates. However, the storage capacity can be greatly increased by the use of low-cost, high-latent energy-of-fusion materials. Since the heat of fusion of most materials is very much larger than their specific heat, heat of fusion has the advantage of compactness in addition to constant temperature operation.

In thermal energy storage subsystems, the use of inorganic phase-change materials and their mixtures and, preferably, eutectic mixtures (because of

their well-defined and sharp melting temperatures), is very attractive for the large-scale storage of thermal energy. There are several problems associated with these materials that must be solved before they can be successfully used for energy storage.

The physical and chemical property data for commercially available salts and their mixtures have been found to be generally inadequate for serious technology assessment. Commercial materials must be considered for any real energy storage application and their thermal stability is of primary concern. Physiochemical properties, which include the heats of fusion, specific heat, density, viscosity and volume change during phase transition, need further investigation. In addition, corrosion to container/heat exchanger and stress corrosion and thermal conductivity data are necessary information for technology assessment. It is important to characterize their thermophysical properties, long-term thermal stability and the effect of impurities and moisture on the thermodynamic properties and thermal stability. It is also necessary to measure the corrosion characteristics of low-cost container/heat transfer materials in molten phase-change materials with a view to understanding the mechanism of corrosion and to suggest methods to minimize corrosion. The information on the thermal conductivity and the volume changes that accompany the fusion of phase-change materials has to be obtained by experimental studies.

Energy conservation can be achieved one way by using less expensive and more reliable energy storage subsystems. These energy storage devices help to expand the amount of currently available energy. Materials research is needed to advance the energy storage technology. These energy storage subsystems can be used to increase base load capacity of existing generators and can store energy more effectively from solar power plants for peak-hour demands as well as for cloudy days. These energy storage devices can offer substantial economic benefits to all sectors of our society. Energy storage is an energy conservation program in that scarce and expensive high-grade oil and gas generators used to meet peak-hour energy demand can be replaced by storing energy during off-peak hours.

In this paper, data on the heats of fusion and specific heats of promising low-cost eutectic mixtures, with melting points in the range of 465-720°C, suitable for thermal energy storage in solar-thermal power program, are presented and compared with the calculated values. It is apparent from the data that lithium salts have the highest energy storage capacity and next in energy storage capacity are the fluoride mixtures of alkali metals and the mixtures of their fluorides and chlorides.

The corrosion of metals and alloys in molten salts has not been studied as extensively as in aqueous systems. However, the forms of corrosion in molten salts are basically the same as those at room temperature, like pitting, selective attack, cracking and uniform corrosion. The major difference in high temperature corrosion is that solid phase diffusion may take place giving rise to a different composition at the reaction interface from the gross composition of the alloy. The corrosivity of molten salts generally increases with time since they can become oxidized and contaminated with metal impurities. The nature of the films formed on ferrous alloys both at ordinary and high temperature is a complex oxide layer. Electron diffraction studies have shown that a wide variety of localized oxidation processes can occur, depending on the environment, the temperature and the composition of the alloy. The stable final oxide is shown to be α -Fe₂O₃.¹ While metals and alloys are virtually insoluble in the non-oxidizing aqueous solutions, metals in fused salts can be appreciably soluble so corrosion can occur without oxidation. Fortunately, metals seem to be appreciably soluble only in their own salts; therefore, corrosion by direct dissolution may not be very important. The corrosion studies described in this paper relate to molten salt eutectic mixtures comprising chlorides, fluorides, and sulfates of alkali and alkaline earth metals. These molten salt mixtures, like most others, are ionic, are thermally stable with low vapor pressure, and have high thermal and electrical conductivities and low viscosities.²

The corrosion studies of stainless steel and mild steel in these melts carried out by weight-loss measurements show that in all these mixtures initially the corrosion rate is high and it drops off very rapidly with time and seems to level off around 30 hours in the case of the fluoride mixture and around 80

hours for the remaining chloride and sulfate mixtures. The corrosion rate is slightly higher for mild steel in these eutectic mixtures, it is about 6 mils/year in KCl-NaCl-Na₂SO₄, about 7 mils/year for BaCl₂-CaCl₂-KCl and 16 mils/year for CaCl₂-KCl-MgCl-NaCl; for stainless steel (304ss), it is about 4 mils/year in KCl-NaCl-Na₂SO₄, and about 4 mils/year in KF-LiF-KCl. The corrosion kinetics follows first a parabolic, then a linear rate-law. A plot of (mg/cm²)² vs time gives a linear relationship corresponding to the parabolic rate law. This behavior suggests that the corrosion process is first controlled by the rate of diffusion of the reactants through the growing oxide layers followed by ionic diffusion through a porous oxide film.

Recent corrosion studies of stainless steel and mild steel in NaNO₃ and KNO₃ based eutectic mixtures carried out around 320°C indicate less than 1 mil/year corrosion rate.³ This low rate of corrosion has been attributed to the formation of passivating iron oxide film formed by sodium nitrate and potassium nitrate melts. The corrosion rate for mild steel in LiCl-KCl at about 380°C is found to be 2.5 mil/year and it has been attributed to the corrosive nature of chloride ion and the presence of water in lithium salts.^{1,3}

As most corrosion processes are electrochemical in nature, in recent years, accelerated electrochemical corrosion test methods have been used increasingly in corrosion studies.

The electrochemical techniques like the potentiodynamic polarization studies and current-potential curves can be used to obtain information on corrosion processes and mechanisms as well as corrosion rates. The electrochemical corrosion of iron and steel in molten salts can be defined in terms of redox potential. This potential depends on the relationship of the activities of the oxidized and reduced species in the molten salt mixture given by:

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{(O_x)}{(R_d)}$$

Where E is the potential of the corroding metal, E° is the equilibrium potential, and O_x and R_d represent the activities of the oxidized and reduced species in the molten salts. Therefore, the metal or the alloy in contact with the molten

salt mixtures takes up a potential, determined by the activity of its ions in solution in the melt.^{2,4}

Accelerated corrosion studies using electrochemical current-potential curves have been made to estimate the corrosion characteristics of the molten salts on ferrous alloys. The corrosion current and corrosion potentials have been measured by accentuating the anodic or cathodic process on the alloy specimen. The potentiodynamic polarization curves have been obtained for mild steel, stainless steel and inconel in these molten salt mixtures and the critical current density for passivation measured. The microscopic examination of the surface as well as the lack of hysteresis in the polarization curve on back-scanning the potential seem to show the absence of pitting corrosion.

Auger electron spectroscopy is being used increasingly in the analysis of the surface layers of solids exposed to different environments.^{5,6} In particular, the surfaces of metals and alloys that have been in contact with the molten salt mixtures can be evaluated for their corrosion resistant behavior using their Auger electron spectra. This method, combined with in-situ sputtering technique, provides a depth-composition profile from which valuable information on the nature of corrosion products, their depth of penetration into the surface and the composition of protective layers formed, can be obtained.

The Auger amplitude vs sputtering time (thickness) for 302ss in the eutectic mixture KF-LiF-NaF shows that the oxide layer thickness amounts to about 5000Å with the chromium and nickel concentration building up and remaining strong. In the case of mild steel, auger amplitude vs sputtering time (thickness) indicates that the oxide layer thickness is not very high and seems to extend to about 4000Å, indicating fairly good corrosion resistance.

The corrosion of ferrous alloys in the melts seems to be initiated with the oxidation of iron by traces of water. According to electrochemical mechanism, iron dissolves in molten salts in the form of Fe^{++} ions as has been demonstrated by several workers⁷ at the anodic site whereas the cathodic reaction could be the reduction of H^+ or H_2O or O_2 . The dissolution potential of Fe to Fe^{2+} is more negative than that for Fe to Fe^{3+} , hence during corrosion, Fe must go into solution as Fe^{2+} at the anodic site of the local cell.

FeO being unstable at temperatures below 600°C and being easily oxidized by traces of water or the corrosive environment giving magnetite which by further oxidation produces hematite. The solubility of iron oxide in the molten salt mixture is small but sufficient to form some concentration of Fe³⁺. The high oxidizing potential of the Fe³⁺/Fe²⁺ system in this medium allows the ferric ion to act as the main depolarizer in the corrosion process.

Thus, the electrochemical approach to corrosion of metals and alloys in molten salts leads to interpretation of the process by the same mechanism as in aqueous solutions, i.e., through local cells. The metal goes into the melt from anodic sites of the lattice, especially at the grain boundaries of the crystal, and the depolarizers are reduced at cathode sites.⁸ These may be CO₂, CO, O₂ and H₂. In lithium fluoride containing eutectic mixtures, it is possible that layers of compounds such as Li(FeCr)O₂ may develop at the alloy-oxide interface.⁹ The various electrochemical reactions responsible for corrosion can be written as:

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HIGH TEMPERATURE THERMAL ENERGY STORAGE

MATERIALS AND THEIR PROPERTIES

Viewgraphs Presented

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PHYSICO-CHEMICAL AND THERMODYNAMIC PROPERTIES OF
FROMISING LOW COST EUTECTICS (mp 450 - 720°C)

SALT MIXTURES	COMPOSITION MOLE %	CALCULATED DENSITY g/cm ³	MEASURED FUSION TEMP (°C)	CALCULATED HEAT OF FUSION KCal/mole	MEASURED HEAT OF FUSION KCal/mole
KCl - KF - LiF	6.5 - 47.5 - 46	2.4781	468	4.44	4.12
KF - LiF - SrF ₂	46.5 - 50.1 - 3.4	2.5837	483	4.6131	4.17
LiF - NaCl	40.5 - 59.5	2.2361	668	3.89	4.59
LiF - NaCl	43 - 57	2.236	684	4.10	4.588
LiCl - LiF - NaCl	63.5 - 19 - 17.5	2.0219	464	4.422	—
BaCl ₂ - KCl - MgCl ₂ - NaCl	8.7 - 52.3 - 18.2	2.2683	475	5.087	5.33
CaCl ₂ - KCl - NaCl	50 - 7.25 - 42.75	2.3319	465	5.535	4.19
KCl - KBr	40 - 60	2.6284	716	5.934	—
KF - LiF - NaF	42.46.5 - 11.5	2.5206	457	4.38	6.2
K ₂ CO ₃ - Li ₂ CO ₃	56 - 44	2.3204	474	4.482	—
BaCl ₂ - CaCl ₂ - KCl	14 - 28.1 - 57.9	2.507	535	5.869	8.6
CaCl ₂ - LiCl	39 - 61	2.1338	480	5.399	4.45
KCl - NaCl - Na ₂ SO ₄	55.1 - 3.5 - 41.3	2.2697	514	5.69	—

THERMAL DATA OF EUTECTICS. (mp 450°C - 720°C)

SALT MIXTURES	$\int_{T_f}^{T_f+10} C_{P_l} dt$ KCal/mole *	$\int_{T_f-10}^{T_f} C_{P_s} dt$ KCal/mole *	MEASURED ΔH_f		CALCULATED Q		
			(Btu/lb)	(Btu/ft ³)	KCal/mole	Btu/lb	Btu/ft ³
KCl-KF-LiF	0.1577	0.11	167.25	21,551	4.708	191.1	24,627
KF-LiF-SrF ₂	0.1613	0.113	128.75	16,197	4.987	150.9	18,983
LiF-NaCl	0.1580	0.11	182.71	19,857	4.158	165.3	17,988
LiF-NaCl	0.1580	0.11	165.71	19,500	4.368	176.8	18,560
LiCl-LiF-NaCl	0.1527	0.107	—	—	4.682	200.2	20,998
BaCl ₂ -KCl-MgCl ₂ -NaCl	0.1799	0.127	110.79	12,941	5.394	112.12	13,097
CaCl ₂ -KCl-NaCl	0.2035	0.142	87.8	11,013	5.88	123.2	15,454
KCl-KBr	0.1660	0.108	—	—	6.202	110.3	13,150
KF-LiF-NaF	0.1582	0.110	270.22	35,510	6.93	302.03	39,692
K ₂ CO ₃ -Li ₂ CO ₃	0.3428	0.27	—	—	5.095	83.45	10,487
BaCl ₂ -CaCl ₂ -KCl	0.1985	0.13	149.6	18,946	6.4685	112.5	16,250
CaCl ₂ -LiCl	0.1980	0.20	115.84	13,083	5.787	150.6	17,016
KCl-NaCl-Na ₂ SO ₄	0.279	0.265			6.234	110.22	16,019

* CALCULATED VALUES

MILD STEEL

→ AUGER AMPLITUDE

MILD STEEL (KF-LiF-NaF)

AUGER AMPLITUDE

MILD STEEL (CaCl_2 -KCl - NaCl)
(ANNEALED)

BOCl₂-KCl-MgCl₂-NaCl @ 500°C
ASTM 285 MILD STEEL W.E.

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Electrochemical and Fuel Storage

ADVANCED BATTERY SYSTEMS

by

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for this presentation

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THE WESTINGHOUSE SULFUR CYCLE
HYDROGEN PRODUCTION PROCESS

Viewgraphs Presented
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WESTINGHOUSE THERMOCHEMICAL HYDROGEN PRODUCTION PROCESS

- ELECTROLYSIS

$$\epsilon^0 = -0.17 \text{ VOLTS}$$

- THERMAL DECOMPOSITION

ADVANTAGES

- HYDROGEN PURITY IS INDEPENDENT OF PROCESS FUELS
- OXYGEN PRODUCTION IS POSSIBLE
- ANY CONVENIENT OR INEXPENSIVE PROCESS FUEL CAN BE EMPLOYED

PROCESS HEAT EXCHANGER

CALENDAR YEAR

..... CONTRACT EX-76-C-01-2262

--- CONTRACT EG-77-C-02-4378

/// CONTRACT ET-78-C-02-4705

MATERIALS CONSIDERATION FOR THE WESTINGHOUSE
SULFUR CYCLE HYDROGEN PRODUCTION PROCESS

by

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MATERIALS CONSIDERATION FOR THE WESTINGHOUSE SULFUR CYCLE HYDROGEN PRODUCTION PROCESS

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ABSTRACT

The Sulfur Cycle Hydrogen Production Process is a hybrid electrochemical/Thermochemical process for decomposing water into hydrogen and oxygen. The thermochemical portion of the process requires the vaporization of concentrated sulfuric acid and subsequent thermal decomposition of the resulting sulfur trioxide. In order to maximize efficiency, the process is carried out at elevated pressures. The acid vaporizer which operates at temperatures of approximately 846°F and the reduction reactor which operates at approximately 1600°F place unique requirements on structural materials. A program to investigate the compatibility of potential candidate structural materials for use in the vaporizer and reduction reactor has been initiated.

INTRODUCTION

The Sulfur Cycle Hydrogen Production Process has been under development at Westinghouse for the past several years. Details of the process have been presented in a number of publications [1 - 7] and two papers at the 2nd World Hydrogen Conference [6 - 7]. The emphasis of this paper is to review the critical material problem areas associated with the thermal decomposition portion of the Sulfur Cycle Hydrogen Production Process and to report on the status of work in progress at Westinghouse to resolve the materials problems.

The thermal decomposition portion of the process is considered to be critical from a materials point of view, because the temperatures and pressures involved depart significantly from standard sulfuric acid handling practice and as a result there is a dearth of information available concerning the compatibility of structural materials with sulfuric acid under these conditions. The acid decomposition loop is shown in a simplified schematic in Fig. 1. Hydrogen is produced at the cathode in the electrolyzer. Sulfuric acid (H_2SO_4) is produced at the anode from sulfurous acid (H_2SO_3). The sulfuric acid from the anode is regeneratively heated to the boiling point, 846°F at 20 atmospheres. The vapor phase is heated further to 1600°F using both regenerative and external heat. As the vapor phase is heated to 1600°F, the molecular sulfuric acid decomposes to water and sulfur trioxide. At 871°C, the process stream passes through a catalyst which expedites the thermal decomposition of sulfur trioxide to sulfur dioxide and oxygen.

The process stream is cooled through a series of heat exchangers which recovers the sensible heat. The state and composition of the process stream as it passes through each of steps shown in Fig. 1 is given below.

In order to carry out the process as shown requires structural materials with unique characteristics. For example, the use of tube-in-shell type heat exchangers for the vaporizer, regenerators and the reduction reactors is highly desirable to maximize heat transfer and to facilitate manufacture. The fabrication of tube-in-shell type heat exchangers requires structural materials which are readily reduced to tube form and are weldable. In addition, the structural material must be compatible with the processes stream. In the regenerators a hostile environment of different composition can be present on each side of the heat transfer surface, i.e., heat exchanger tubes. In the preheater, sulfuric acid in liquid form is present with condensed sulfuric acid containing SO_3 with SO_2 and O_2 present in the gas phase. A similar situation exists for the acid vaporizer, where boiling sulfuric acid exists on one side and steam, SO_3 , SO_2 , and O_2 are present on the other. In the reduction reactor, the heat transfer media from the external heat source is present on one side while steam, SO_3 , SO_2 , and O_2 is present in the process stream along with the catalyst. Thus, the structural materials of each component are exposed to a variety of conditions. The two regions where material compatibility with process stream are considered to be most critical are in the acid vaporizer and the reduction reactor. In the acid vaporizer, sulfuric acid, which ranges from 80 to 98 per cent (azeotrope) concentrated, is converted from liquid to the vapor state. At concentrations below the azeotrope (98%), water is driven off in preference to sulfuric acid. The stream increases in acid concentration until the azeotrope concentration is achieved and the liquid phase is then completely converted to the vapor state. This type of boiling which occurs over a temperature range is more conducive to tubular type heat exchangers.

In the reduction reactor not only is compatibility of structural material with the process stream important, compatibility with the catalyst is also critical. Poisoning of the catalyst by corrosion products and undesirable interaction of the catalyst with the structural material are factors which must be defined before selection of a catalyst or structural material can be made. Initial catalyst screening efforts are aimed at evaluating commercially available catalysts for the reduction of SO_3 . Compatibility evaluation of the most promising catalysts with structural materials is planned. The major areas of concern with respect to structural material process stream compatibility which will be discussed in this paper involve the acid vaporizer and the SO_3 reduction reactor.

STATUS OF MATERIALS CURRENTLY USED FOR HANDLING SULFURIC ACID

The most logical starting point in the consideration of potential structural materials for the Sulfur Cycle Hydrogen Production Process is the experience gained in the sulfuric acid manufacturing industry.

The compatibility of the most common structural materials for sulfuric acid service is summarized in Table 1. The data are given for various acid concentration with upper temperature limits noted. In those cases where the boiling point is indicated, it is assumed to be one atmosphere. Of the materials which appear in the table, only a few are suitable for use with acid at concentrations above 80 percent. Temperature limitations reduce the number of candidate materials even further. The materials with the highest probability of surviving the conditions encountered in the sulfur cycle water decomposition cycle are listed below, along with comments concerning suitability with respect to requirements listed previously.

Precious Metals

Gold, platinum and their alloys are noted for their resistance to acid attack to very high temperatures [9]. Their cost restricts their use to thin clads on less expensive substrates. The use of precious metals in the water decomposition system is not considered because of the associated economic burden.

Tantalum and Its Alloys

The use of this refractory metal in acid service is increasing. At acid concentrations below 80 percent and temperatures below 375°F, the excellent corrosion resistances more than offset the relatively high cost of this material. However, at acid concentrations above 80 percent tantalum has a tendency to become embrittled due to hydrogen pickup. Experimental work by Sterns and Bishop has shown that precious metal rivets are effective in eliminating hydrogen embrittlement of tantalum exposed to 85 percent concentrated acid at 485°F [10].

Alloys with High Silicon Content

Metallic alloys with high silicon content, such as Hastelloy U, Duriron, Durimet, and Cholorimet, are the standard structural materials used in the sulfuric acid industry today [8, 12]. These materials are primarily casting alloys which are brittle, not readily joined by welding and are also notch sensitive. Consequently, these materials are not normally utilized in a structural load-bearing capacity.

The effect of silicon content on the corrosion resistance of iron and steel is illustrated in Figs. 2 and 3 [13]. In Figure 2, the corrosion rate of steel is shown as a function of acid concentration for a number of temperatures. In Figure 3, the corrosion behavior of Duriron, a cast iron with approximately 15 percent silicon, is shown at the boiling temperature as a function of acid concentration. A corrosion rate of 5 mils per year is indicated at the boiling point for concentrations above 80 percent. This corrosion rate is lowest reported data for non-precious metal. The effect of higher temperatures due to higher system pressure and the resulting increase in boiling point of the acid is currently under investigation.

Glass and Glass Lined Steel

Glass or glass lined steel is commonly used for handling acid in the chemical industry. The behavior of glass in contact with sulfuric acid at various concentrations is shown in Fig. 4 as a function of temperature [14]. Above 80 percent concentration, glass is not resistant to attack at the acid boiling point. The reason for this behavior is shown in Fig. 5 which shows the effect of superheated water on the corrosion of Pyrex glass. As the temperature increases above 400°F, the silica in the glass becomes hydrated, forming H_2SiO_3 , which is soluble in superheated water. Thus, the incompatibility is not with sulfuric acid, but with water, a decomposition product. Pyrex, according to Corning, is their most corrosion resistant glass. As indicated by the curve in Fig. 5, the corrosion rate approaches 0.3 inch per year as the temperature nears 400°F and presumably continues to increase above 400°F. This corrosion rate is unacceptable for long time applications.

Fluoropolymers (Teflon, Kynar)

Polymers such as Teflon exhibit excellent resistance to acid attack at all concentrations up to 400°F where thermal decomposition begins to occur. Polymers are used as liners on structural materials where loads are encountered [13].

Acid Proof Brick

Acid proof brick is the most widely used non-metallic material for construction of sulfuric acid plants [13]. The bricks are used to line carbon steel shells. The lining serves to reduce temperatures at the surface of the metallic vessel. The brick linings are usually backed up by a polymer or asphaltic mastic to protect the metallic liner from acid seepage through the brick-work. Recent advances in mortars have helped in overcoming swelling, a problem encountered in mist acid conditions or where frequent filling and emptying occurs. Special construction techniques have been used to overcome the swelling problem. Acid proof bricks have been used at temperatures as high as 600°F. With proper construction techniques higher temperatures are possible.

The pertinent characteristics of available materials with known compatibility with sulfuric acid is summarized in Table 2. Precious metals meet all the prerequisites, however, their very high cost for this application is prohibitive.

High silicon containing alloys, such as Duriron have acceptable corrosion rates up to the boiling point under normal atmospheric pressures. Corrosion rates at higher pressures must be determined. Methods for joining the cast material to provide leak tight joints must be developed. Glass, because of its poor compatibility with superheated water, must be restricted to use at temperatures below 300°F. Polymers are restricted because of their thermal instability at temperatures above 400°F. Acid proof brick, because of its insulating properties, makes an excellent liner or barrier material for reducing temperatures between the process stream and the pressure vessel wall.

MATERIALS FOR USE IN THE HIGH TEMPERATURE-DISSOCIATED SULFURIC ACID ENVIRONMENT

In the high temperature portion of the thermal decomposition process, four components make up the process stream. They are H_2O , SO_2 , SO_3 , and O_2 . Of these components, SO_2 and H_2O are considered to be most potentially corrosive with respect to structural materials. SO_2 is known to react with nickel in alloys to form porous nickel sulfide (Ni_3S_2). The nickel sulfide hinders formation of oxides of nickel and chromium required for protection of the alloy. In corrosion studies by Hancock involving nickel-chromium alloys in sulfur containing atmospheres in the temperature range 1100 to 1650°F, it was found that pure SO_2 can attack nickel chromium alloys at 1650°F through the formation of a nickel sulfide scale [15]. However, when the chromium level was increased only NiO and Cr_2O_3 were formed at the surface and the corrosion rate remained at an acceptably low level. Similar corrosion studies conducted by Viswanathan and Spengler [16] using an 85 Ni-15 Cr alloy exposed at 1600°F to a controlled atmosphere containing O_2 , SO_2 , SO_3 , and N_2 also revealed that severe sulfidation of Ni-Cr alloy can occur by direct reaction of SO_2 with the base metal as reported by Hancock. It was also determined that the most severe attack occurred at an SO_2 concentration level of 0.2 percent SO_2 in nitrogen, as shown in Fig. 6. As the SO_2 concentration increased above 1 percent the severity of attack diminished. The addition of oxygen at a level as low as 100 ppm was found to completely eliminate the severe sulfidation which occurred at the 0.2 percent SO_2 level. Further reduction in corrosion rate by a factor of 300 was noted when the oxygen level was increased to 2 per cent. Additions of SO_3 to the gas mixture further decreased the corrosion rate. The presence of O_2 and SO_3 apparently enhances the formation of protective Cr_2O_3 and NiO at the surface while retarding the formation of Ni_3S_2 . Alkali metals, which expedite the hot corrosion phenomena are not expected to be present in the process stream, and thus, are not expected to be a factor in the compatibility of structural materials with the process stream. The experimental evidence noted, although limited, gives indication that the SO_2 , SO_3 , and O_2 components of process stream may be contained by a properly selected structural material.

The other major area of concern with regard to compatibility of the process stream with structural materials at elevated temperatures involves superheated steam, a major constituent of the process stream. The process stream entering the reduction reactors is composed of 34.7 percent H_2O and 65.3 percent SO_3 by weight [11]. Maximum operating pressure is 300 psig.

Published data on the corrosion behavior of superheater alloys in high temperature-high pressure steam is limited to great extent to temperatures below 1500°F with most data available in the 1000 to 1200°F temperature range. Alloys which have received the most attention are the austenitic stainless steels, Inconel 600, Inconel 625, Incoloy 800, chromium-nickel steels, and the ferritic low alloy chromium-molybdenum (croloy) steels. Several studies have been conducted in which the corrosion behavior of superheater tube materials in the temperature range 1350 to 1500 has been evaluated [17, 18]. In these studies which were sponsored by the ASME Research Committee on High Temperature Steam Generation, scale build up as a function of exposure for 12 and 18 months to 2000 psig steam was reported. Typical results are reported in Tables 3 and 4. Reported scale thicknesses are an average of number of measurements. Scale does not appear to increase significantly as a function of time. Test results for materials exposed to temperatures up to 1751°F for 5000 hours indicate no loss after descaling for highly alloyed stainless steels as given in Table 5 [19]. The conventional 18 Cr-8 Ni and the niobium stabilized version exhibited no loss up to 1625°F. Work in Sweden at temperatures up to 1482°F showed essentially the same results as those found in the ASME testing, in that the higher alloyed materials performed better [20].

Some data on very high temperature (2200°F) steam corrosion have been reported [21] and are included in Table 5. Although the data are only for a short time (312 hours) and for a low pressure (near 20 psi), they are valuable in that they permit qualitative comparisons to be made among the alloys tested. It is apparent from these data that the best corrosion resistance under the conditions studied is possessed by Incoloy 800 and Hastelloy X. Both alloys were superior to Inconel 600.

It is significant that on tests performed with Inconel 600 and Hastelloy X at 2000 and 2200°F the differences found between rates of attack by steam and air are negligible. Also, the scales formed by each atmosphere were identical, being composed mainly of a $\text{NiO} \cdot \text{Cr}_2\text{O}_3$ type spinel.

A number of investigators reported that steam corrosion for many alloys was no more severe than air corrosion at a given temperature, particularly at temperatures above 1300 to 1400°F.

While corrosion compatibility with the process stream for reduction reactor materials has been emphasized here, it is recognized that other factors such as creep behavior and thermal stability of candidate structural materials must also be considered in the selection of reduction reactor materials.

EXPERIMENTAL MATERIALS PROGRAM AND SCHEDULE

Due to lack of available information on the compatibility behavior of materials in contact with sulfuric acid in both the liquid and vapor phases at elevated temperatures and pressures, a materials test program was initiated at the Westinghouse Advanced Energy Systems Division under DOE-sponsorship to identify structural materials for the various critical components of the Sulfur-Cycle Hydrogen Production Process. The acid vaporizer and the reduction reactor were identified as critical components with respect to materials compatibility with the process stream. In the acid vaporizer, regenerative heat must be supplied to the process stream to convert the liquid sulfur acid to the vapor state. Liquid-vapor interfaces or boiling zones, historically are regions which are susceptible to accelerated corrosive attack. In the reduction reactor, the containment material is exposed to a process stream containing H_2O , SO_2 , and O_2 at $1600^{\circ}F$ in the presence of a catalyst.

The material test programs are outlined in Tables 7 and 8.

Screening tests are currently underway in each area to identify candidate materials for endurance testing under dynamic conditions. An integrated scaleup loop utilizing the most promising materials identified in the screening and endurance investigations will be used to confirm the final selection of containment materials for the critical components of the process. A proposed schedule is shown in Figure 7. The timing of the materials test program is aimed at providing identification of materials for bench scale PDV. Design of this unit is currently scheduled to begin in mid-1982.

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TABLE I TEMPERATURE LIMITATIONS OF SOME COMMON STRUCTURAL MATERIALS USED FOR HANDLING SULFURIC ACID*

MATERIALS	0-10% H ₂ SO ₄	10-50% H ₂ SO ₄	50-60% H ₂ SO ₄	60-75% H ₂ SO ₄	75-90% H ₂ SO ₄	90-98% H ₂ SO ₄	98-100% H ₂ SO ₄
Cast Iron					to 175°F	to 225°F	
High Silicon Cast Iron	to b.p.	to b.p.	to b.p.	to b.p.	to b.p.	to b.p.	to b.p.
Durimet 20	to b.p.	to 176°F	to 176°F	to 150°F	to 150°F	to 176°F	to 176°F
Chlorimet 283	2 to b.p. 3 to b.p.	2 to b.p. 3 to 200°F	2 to b.p. 3 to 200°F	2 to 250°F 3 to 175°F	2 to 250°F 3 to 175°F	2 to 250°F 3 to 225°F	2 to 250°F 3 to 250°F
Hastelloy Alloys B, C, D, F	B to b.p. C to b.p. D to b.p. F to 150°F	B to b.p. C to 200°F D to b.p. F to 150°F	B to b.p. C to 200°F D to b.p. F to 150°F	B to 250°F C to 175°F D to b.p. F - not recommended	B to 250°F C to 175°F D to b.p. F - not recommended	B to 300°F C to 200°F D to b.p. F - not recommended	B to 300°F C to 200°F D to b.p. F - not recommended
Lead	to b.p.	to 400°F	to 400°F	to 400°F	to 85%, 350°F to 90%, 250°F	to 96%, 140°F	
Carpenter Stainless 20 Cb-3	to 5% 150°F						
Platinum, Gold Pt-Au Alloys	to b.p.	to b.p.	to b.p.	to b.p.	to b.p.	to b.p.	to b.p.
Tantalum	to b.p.	to b.p.	to b.p.	to b.p.	to 150°F	to 150°F	to 150°F
Carbon and Graphite	to 340°F	to 340°F	to 340°F	to 340°F	to 340°F	to 96%, 340°F	
Monel, Copper, 10% Alum. Bronze	to 200°F in absence of oxygen	to 200°F in absence of oxygen	to 200°F in absence of oxygen				
Fluoropolymers (Teflon)	to 400°F	to 400°F	to 400°F	to 400°F	to 400°F	to 400°F	to 400°F
Acid Proof Brick	to 600°F	to 600°F	to 600°F	to 600°F	to 600°F	to 500°F	to 600°F

*See also Table II.

TABLE 1 TEMPERATURE LIMITATIONS OF SOME COMMON STRUCTURAL
MATERIALS USED FOR HANDLING SULFURIC ACID* (CON'T.)

Material	Composition (%)
Duriron	Fe-14.5 Si-0.5 Cr-0.5 Mo-1.5 Mn
Hastelloy B	Ni-28 Mo-5 Fe-2.5 Co-1 Cr
Hastelloy C	Ni-16 Mo-16 Cr-6 Fe-2.5 Cr-4 W
Hastelloy D	Ni-9 Si-3 Cu-1.5 Co-2 Fe-1 Cr
Hastelloy F	Ni-20 Fe-22 Cr-6.5 Mo-1 W-2.5 Co-2 Ta + Cb
Carpenter 20 Cb 3	Fe-20 Cr-35 Ni-3 Mo-1 Nb-1 Si
Durimet	Fe-21 Cr-29 Ni-2.5 Mo-3.5 Cu-1.5 Si
Chlorimet 2	Ni-1 Cr-32 Mo-1.0 Si-3 Fe
Chlorimet 3	Ni-18 Cr-18 Mo-1.0 Si-3Fe

TABLE 2. SUMMARY OF CHARACTERISTICS OF AVAILABLE MATERIAL FOR USE IN SULFURIC ACID LOOP

Materials	Compatibility With H_2SO_4	Compatibility With Superheated Water, SO_3 & SO_2	Strength	Fabricability	Joinability	Thermal Conductivity	Relative Cost
Precious Metals (Gold, Platinum)	Excellent	Excellent	Fair	Must be used as clad on substrate	Good	Excellent	Very High
Metals High in Silicon (Duriron)	Excellent	Poor	Fair	Available as castings	Poor	Fair	Moderate
Glasses (Pyrex)	Excellent below 422K	Poor	Poor	Must be used on metal substrate	Poor	Poor	Low
Polymers (Teflon)	Excellent below 478K	Poor	Poor	Must be used on metal substrate	Good	Poor	Low
Acid Proof Bricks	Excellent	Excellent	Fair	Available as bricks and simple shapes	----	Poor	Low

TABLE 3 SCALE THICKNESS ON ALLOYS EXPOSED TO 1500°F STEAM REF. 7

<u>Material</u>	<u>Exp. Time (months)</u>	<u>Inner Scale (mils)</u>	<u>Outer Scale (mils)</u>	<u>Total (mils)</u>
304 SS	12	2.8	1.6	4.4
321 SS	12	5.0	1.0	6.1
	18	3.1	0.8	3.9
316 SS	12	3.0	1.2	4.2
	18	1.9	2.0	3.9
16Cr-25Ni-6Mo	6	0.3	1.3	1.6
	12	1.6	1.1	2.7
17Cr-14Ni-CuMo	6	0.3	1.7	2.0
Croloy 15-15N	12	7.8	1.0	8.8
	18	5.6	1.4	7.0

TABLE 4 AVERAGE SCALE THICKNESS (mils)* Ref. 18

<u>Alloy</u>	<u>1200°F</u>		<u>1350°F</u>		<u>1500°F</u>	
	<u>12 months</u>	<u>18 months</u>	<u>12 months</u>	<u>18 months</u>	<u>12 months</u>	<u>18 months</u>
304 SS	1.0	1.2	3.7	3.9	2.4	N.O.**
321 SS	1.2	3.3	1.1	0.8	5.2	N.O.
347 SS	0.6	0.7	0.7	0.7	N.O.	N.O.
310 SS	0.3	0.2	0.3	0.5	N.O.	N.O.
17Cr-14Ni-CuMo	5.0	3.7	0.8	6.8	N.O.	N.O.
16Cr-25Ni 6Mo	1.6	2.8	1.0	1.2	1.0	N.O.
Inconel 600	0.3	0.1	0.4	0.3	N.O.	N.O.
Incaloy 800	0.6	0.7	0.7	0.7	N.O.	N.O.
316 SS	4.0	3.6	2.8	3.0	1.7	2.0
Croloy 15-15N	4.5	4.2	3.3	4.8	6.8	5.7

* Tubes having dimensions 2.0 in. OD x 1/2 in. wall x 42 in. length were used to carry steam of 2,000 psig pressure.

** Not obtained

TABLE 5 CORROSION OF STEEL BARS IN CONTACT WITH STEAM FOR 500 HR REF. 19

Steel	Steam Temp. (°F)	Descaled	
		Wt. Loss 1/2" dia bar-%	
18Cr-8Ni SS	1475	0	
	1506	0	
	1675	0	
18Cr-8Ni-Nb SS	1470	0	
	1508	0	
	1560	0	
	1675	0	
	1728	12.3	
	1765	11.5	
25Cr-20Ni SS	1751	0	
25Cr-15Ni-2W	1751	0	

TABLE 6 OXIDATION RATES FOR STAINLESS STEELS AND SUPER ALLOYS IN 2000°F and 2200°F STEAM

Deduced Alloy Designation	Composition								Oxidation Rate* (mils/year)
	Cr	Ni	Fe	Mo	W	Co	Nb	Cu	
1. Inconel 600	15	78	7	--	--	--	--	--	268
2. 20Cb-3	20	29	45	2	--	--	0.8	3	**
3. Hastelloy X	22	51	18	9	--	--	--	--	146
4. Incoloy 800	25	35	40	--	--	--	--	--	125
5.	25	45	21	3	3	3	--	--	210
6.	25	41	15	--	4	15	--	--	210
7. 310 SS	25	20	55	--	--	--	--	--	268
8.	30	20	50	--	--	--	--	--	223

* Calculated from original weight and weight after descaling. These oxidation rates would apply only to first several 1000 hours of operation since oxidation rates beyond this time period generally decrease appreciably.

** Rapidly attacked following 80 hours in 2000°F steam and thus not tested at 2200°F.

TABLE 7 ACID VAPORIZER MATERIALS TEST PROGRAM

<u>TEST TYPE</u>	<u>TEST ENVIRONMENT</u>	<u>SAMPLE LOCATION</u>	<u>TEMP °F</u>	<u>PRESSURE (ATMOS)</u>	<u>TEST TIME</u>
MATERIALS SCREENING	98% H ₂ SO ₄ (REFRESHED)	LIQUID, VAPOR LIQUID-VAPOR INTERFACE	680 846	3.4 (50 PSI) 20.0 (300 PSI)	250-HOUR INCREMENTS 1000-HOURS TOTAL
MATERIALS LIFE	98% H ₂ SO ₄ (REFRESHED)	LIQUID, VAPOR LIQUID-VAPOR INTERFACE	680 846	3.4 (50 PSI) 20.0 (300 PSI)	250-HOUR INCREMENTS 5000-HOURS TOTAL

TABLE 8 REDUCTION REACTOR MATERIAL TEST PROGRAM

<u>TEST TYPE</u>	<u>TEST ENVIRONMENT</u>	<u>TEST TEMPERATURES °F</u>	<u>PRESSURE</u>	<u>TEST TIME</u>
MATERIALS SCREENING	SO ₃ , STEAM AND ARGON	900, 1200 AND 1000°F	ATMOSPHERIC	100-HOUR INCREMENTS TOTAL TIME 500-HOURS
MATERIAL LIFE	SO ₃ , STEAM AND ARGON	900 AND 1600°F	ATMOSPHERIC	100-HOUR INCREMENTS TOTAL TIME 5000-HOURS

Figure 1. Simplified Schematic of H_2SO_4 Decomposition Loop

Figure 2. Corrosion of Steel by Sulfuric Acid, General Chemical Data (Ref. 13)

Figure 3. Corrosion Rate of Duriron in Sulfuric Acid (Ref. 13)

Figure 4. Corrosion Rate of Glass-Lined Steel in Sulfuric Acid
(Ref. 13)

Figure 5. Effect of Superheated Water on Corrosion of Pyrex Glass (Corning No. 7740) (Ref. 14)

Figure 6. Variation of Amount of Corrosion with Concentration of SO₂ in SO₂-N₂ Atmosphere

Figure 7. Sulfur Cycle Materials Test Program Schedule

MATERIALS CONSIDERATION FOR THE WESTINGHOUSE
SULFUR CYCLE HYDROGEN PRODUCTION PROCESS

Viewgraphs Presented

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SULFURIC ACID THERMAL DECOMPOSITION PROCESS

SUMMARY OF CHARACTERISTICS OF AVAILABLE MATERIAL FOR USE IN SULFURIC ACID LOOP

Materials	Compatibility With H_2SO_4	Compatibility With Superheated Water, SO_3 & SO_2	Strength	Fabricability	Joinability	Thermal Conductivity	Relative Cost
Precious Metals (Gold, Platinum)	Excellent	Excellent	Fair	Must be used as clad on substrate	Good	Excellent	Very High
Metals High in Silicon (Duriron)	Excellent	Poor	Fair	Available as castings	Poor	Fair	Moderate
Glasses (Pyrex)	Excellent below 300°F	Poor	Poor	Must be used on metal substrate	Poor	Poor	Low
Polymers (Teflon)	Excellent below 400°F	Poor	Poor	Must be used on metal substrate	Good	Poor	Low
Acid Proof Bricks	Excellent	Excellent	Fair	Available as bricks and simple shapes	----	Poor	Low

AREAS OF WORK

ELECTROLYSIS

ELECTROCATALYSTS

ELECTRODES

SO₃ REDUCTION - CATALYSTS

SO₃ REDUCTION - MATERIALS

ACID VAPORIZER - MATERIALS

MATERIALS DEVELOPMENT PROGRAM FOR THE SULFUR CYCLE
WATER DECOMPOSITION PROCESS

VAPORIZER MATERIALS

- STATIC SCREENING TESTS
 - ALL CANDIDATE MATERIAL
 - PRESSURIZED TESTS AT TEMPERATURE
- DYNAMIC TESTING
 - SELECTED CANDIDATE MATERIALS
 - PRESSURIZED TESTS AT TEMPERATURE

REDUCTION REACTOR MATERIALS

- INLET CONDITIONS (H_2O , SO_3)
 - ATMOSPHERIC
 - PRESSURIZED
- OUTLET CONDITIONS (H_2O , O_2 , SO_3 , SO_2)
 - ATMOSPHERIC
 - PRESSURIZED
- CATALYST COMPATIBILITY

INTEGRATED SCALEUP LOOP

- COMBINED ACID VAPORIZER AND REDUCTION REACTOR

<u>TEST TYPE</u>	<u>TEST ENVIRONMENT</u>	<u>SAMPLE LOCATION</u>	<u>TEMP °F</u>	<u>PRESSURE (ATMOS)</u>	<u>TEST TIME</u>
MATERIALS SCREENING	98% H ₂ SO ₄ (REFRESHED)	LIQUID, VAPOR	680	3.4 (50 PSI)	250-HOUR INCREMENTS
		LIQUID-VAPOR INTERFACE	846	20.0 (300 PSI)	1000-HOURS TOTAL
MATERIALS LIFE	98% H ₂ SO ₄ (REFRESHED)	LIQUID, VAPOR	680	3.4 (50 PSI)	250-HOUR INCREMENTS
		LIQUID-VAPOR INTERFACE	846	20.0 (300 PSI)	5000-HOURS TOTAL

ACID VAPORIZER MATERIALS TEST PROGRAM

TEST MATERIALS

316 STAINLESS STEEL (1)
 INCONEL 625 (1)
 1018 CS (1)
 HASTELLOY E2
 HASTELLOY C276
 HASTELLOY G
 ZIRCONIUM
 INCONEL 657
 INCOLOY 825
 DURIRON
 DURICHLOR 51
 TANTALUM
 CARTECK-20CB 3
 USS-18-18-2
 310 STAINLESS STEEL
 AL₂O₃ (HOT PRESSED)
 VITREOUS CARBON
 SiC (HOT PRESSED)
 Si₃N₄ (HOT PRESSED)
 SiC (VAPOR DEPOSITED)
 SIALON
 CERVET

FE-18CR-12NI-2Mo-2.0Mn
 NI-22CR-9Mo-5Fe-4Nb
 FE
 NI-28Mo-1Co-1Cr
 NI-16CR-16Mo-4W-6Fe-2.5Co
 NI-23CR-7Mo-1W-20Fe-2.5Co
 Zr
 NI-48CR-1.6Nb-1Fe
 FE-46NI-22CR-3Mo
 FE-14.5Si-0.5Cr-0.5Mo-1.5Mn
 FE-14.5Si-4.5Cr-0.5Mo-0.7Mn
 TA
 FE-20CR-35NI-3Mo-1Nb-1Si
 FE-18CR-18NI-2Si
 FE-26CR-22NI-2Mn
 AL₂O₃
 C
 SiC
 Si₃N₄
 SiC
 Si₃N₄-ALN-AL₂O₃-SiO₂
 SILICA-KEATITE-MULLITE

(1) SAMPLES ALSO ALONIZE COATED

ACID VAPORIZER MATERIALS SAMPLE HOLDER

DURIRON PRESSURE VESSEL FOR EVALUATING
ACID VAPORIZER MATERIALS

BEFORE

AFTER

BEFORE

AFTER

<u>TEST TYPE</u>	<u>TEST ENVIRONMENT</u>	<u>TEST TEMPERATURES °F</u>	<u>PRESSURE</u>	<u>TEST TIME</u>
MATERIALS SCREENING	SO ₃ , STEAM AND ARGON	900, 1200 AND 1000°F	ATMOSPHERIC	100-HOUR INCREMENTS TOTAL TIME 500-HOURS
MATERIAL LIFE	SO ₃ , STEAM AND ARGON	900 AND 1600°F	ATMOSPHERIC	100-HOUR INCREMENTS TOTAL TIME 5000-HOURS

REDUCTION REACTOR MATERIALS TEST PROGRAM

REDUCTION REACTOR MATERIALS SAMPLES IN QUARTZ HOLDER

SULFUR CYCLE MATERIALS TEST PROGRAM SCHEDULE

CONCLUSIONS

- CRITICAL MATERIAL PROBLEM AREAS HAVE BEEN IDENTIFIED
- INITIAL MATERIALS SCREENING TESTS HAVE BEEN INITIATED
- MUCH WORK REMAINS TO BE ACCOMPLISHED IN ORDER TO IDENTIFY COMPONENT REFERENCE MATERIALS
- YOUR SUPPORT AND IDEAS ARE SOLICITED

CORROSION OF CAST ALLOYS IN 70% H_2SO_4
(<0.1 ft/sec)

CHEMICAL COMPOSITION OF CAST ALLOYS

Alloy	Percent										
	<u>C</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Si</u>	<u>Cu</u>	<u>Cb</u>	<u>Ti</u>	<u>Fe</u>	<u>Mn</u>	<u>Other</u>
Results of Specific Chemical Analyses											
304SS Cast	0.060	17.74	8.63	0.30	0.82	0.10	-	-	Bal	-	-
316SS Cast	0.041	19.58	9.69	2.16	1.50	0.07	0.10	0.08	Bal	-	-
Durimet 20 Cast	0.061	19.26	31.53	2.28	1.05	1.06	0.10	0.10	Bal	-	-
Hastelloy B Cast	0.046	0.44	62.11	26.63	0.76	0.10	-	-	-	-	-
Hastelloy C Cast	0.078	15.27	56.45	17.51	0.79	0.09	-	-	-	-	-
Worthite	0.12	17.21	25.66	2.79	3.02	0.58	-	-	Bal	-	-
LaBour R-55	0.036	24.74	52.01	7.77	4.05	0.91	-	-	Bal	-	-
Elcomet K	0.078	16.63	27.16	2.89	1.91	2.56	-	-	Bal	-	-
Illium B	0.031	27.99	52.75	8.76	3.25	6.05	-	-	-	-	-
Illium P	0.22	25.80	8.17	2.11	0.80	2.73	-	-	-	-	-
Illium 98	0.29	29.87	54.76	9.00	0.76	5.40	-	-	-	-	-
3. Nominal Compositions											
Dureco D-10	-	23.00	57.00	4.00	-	8.00	-	-	-	1.00	W 2.00
Durichlor	0.85	-	-	3.00	14.5	-	-	-	Bal	0.65	-
Duriron	0.85	-	-	-	14.5	-	-	-	Bal	0.65	-
Hastelloy D	0.12	1.00	85.	-	8.50- 10.00	2.00- 4.00	-	-	2.00	0.50- 1.25	Co 1.50

Resistance of Hastelloy C-276 to Sulfuric Acid

Corrosion by Five Weight Percent Sulfuric Acid

Temp. °F (°C)	Hastelloy C-276		Hastelloy B	
	a	b	a	b
150 (66)	<1	<1	5	6
175 (80)	1.2	1.3	7	7
214 (Boil) (101)	18	22	2	2
250 (121)	61	67	30	32
300 (149)	100	104	38	43

A. Asphahani
Stellite Division
Cabot Corp.

Results of Corrosion Tests in 10% Sulfuric Acid

Corrosion Rate (Mil Per Year)

<u>Material</u>	<u>Boiling Point 104°C (220°F)</u>	<u>220°C (390°F)</u>
Hastelloy B	2	120
Hastelloy C	50	1140
317 stainless steel	--	2000
Carpenter No. 20	24	2600
Molybdenum	nil	nil
Tantalum	nil	0.2
Silver	0.4	168

Effect of Temperature and
Oxygen Concentration on Corrosion
by Hydrochloric Acid

(Tests made in sealed glass tubes under 2000 psi pressure)

C		Corrosion Rate - Mils Per Year			
Temperature		Hastelloy B		Hastelloy C	
°F	°C	100% N ₂ Atmosphere	80% N ₂ -20% O ₂ Atmosphere	100% N ₂ Atmosphere	80% N ₂ -20% O ₂ Atmosphere
10 Wt Percent HCl					
156	69	-	85	-	114
212	100	9	262	228	293
275	135	20	402	-	>1000
25 Wt Percent HCl					
156	69	2	58	40	91
212	100	8	155	612	449
275	135	49	336	-	>1000

Ref: Corrosion Resistance of Union
Carbide Alloys, December, 1966

Behavior of Stressed Coupons in
Chloride Solutions at 141°C (285°F)

(One Month Exposures)

Alloy	2 Wt% NaCl	<u>Corrosion Rate, Mils Per Year</u>		
		0.8%NaCl +0.2%H ₃ PO ₄	4%NaCl +1.7%H ₃ PO ₄	0.8%NaCl +0.5%CH ₃ COOH
304	0.8 ³	5.6* ^{1,2}	6.1 ^{1,2}	1.2 ^{1,3}
304L	3.3 ³	3.9* ^{1,2}	5.4 ^{1,2}	0.8 ^{1,3}
316		0.7* ^{1,2}	4.4 ^{1,2}	0.3 ^{1,3}
316L		0.3* ¹	1.8 ¹	<0.1*** ^{1,3}
Carpenter 20cb3		2.9** ^{2,3}	3.0 ^{2,3}	<0.1
Incoloy 825		1.1** ^{2,3}	<0.1	<0.1
Haynes 20MOD	<0.1	<0.1**	<0.1	<0.1
Hastelloy G	<0.1	<0.1**	<0.1	<0.1
Hastelloy C-276	<0.1	<0.1**	0.3	<0.1

Notes:

1. Stress corrosion cracking
2. Crevice corrosion
3. Pitting

* 10 days only

** Autoclave leaked last 20 days, exact environment not known

** One specimen out of two cracked

Reference: "Effect of Acids on the Stress Corrosion Cracking of
Stainless Materials in Dilute Chloride Solutions,
A. I. Asphahan, Stellite Div., Cabot Corp.

NOMINAL CHEMICAL COMPOSITION (Weight Percent)

<u>ALLOYS</u>	<u>Fe</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Mn</u>	<u>Si</u>	<u>Cu</u>	<u>C</u>
304	Bal	9	19	-	2*	1*	-	0.05
304L	Bal	9	19	-	2*	1*	-	0.03*
316	Bal	12	17	2.5	2*	1*	-	0.05
316L	Bal	12	17	2.5	2*	1*	-	0.03*
(1) Carpenter 20 Cb3	Bal	33	20	2.5	2*	1*	3	0.04
(2) Incoloy 825	30	Bal	21	3	1*	0.5*	2	0.04
(3) HAYNES alloy No. 20 Mod.	Bal	26	22	5	2.5*	1*	-	0.05*
(3) HASTELLOY alloy G	20	Bal	22	7	1.5	1*	2	0.05*
(3) HASTELLOY alloy C-276	5	Bal	16	6	1*	0.8*	-	0.02*

* Maximum

(1) Registered Trademark of Carpenter Technology Corporation

(2) Registered Trademark of International Nickel Company, Inc.

(3) Registered Trademark of Cabot Corporation

CORROSION RESISTANCE OF GLASTEEL 3300

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ROOM TEMPERATURE AQUEOUS BATTERIES

Viewgraphs Presented

by

Leonard Nanis

SRI International

Menlo Park, California

ZINC-CHLORINE

ENERGY DEVELOPMENT ASSOCIATES

THEO: 99.6 $\frac{\text{A-H}}{\text{LB}}$; 211 $\frac{\text{W-H}}{\text{LB}}$; 465 $\frac{\text{W-H}}{\text{KG}}$; $E_0 = 2.12\text{V}$

$\text{Cl}_2 + 6\text{H}_2\text{O}$; 9.6°C ; DAVY, 1811

Cl_2 ; 5.8 ATM., 20°C . CELL ; MARCONI 1921

DEC 1978 - 45 KWH
CHARGE = 2.26V; DISCH. = 1.95V

170 $\frac{\text{WH}}{\text{KG}}$; 75% EFF

PROBLEMS

POS. GRID CORROSION, CO_2

ZINC DENDRITES, Pe^{++} ADDITIVE, GRAPHITE TYPE

H_2 GASSING (NEG), MORE CN DISCH. UV RECOMB.

GRAPHITE ELECTRODE CONSTRUCTION, ADHESIVES

CASE MATERIALS, PLASTICS KYNAR

ALTERNATIVE Cl_2 STORAGE

SHUTTING CYCLE TO REMOVE ZN. 0.0V CELL

THEO. 37.9 $\frac{\text{A-H}}{\text{LB}}$; 77.3 $\frac{\text{W-H}}{\text{LB}}$; 170.2 $\frac{\text{W-H}}{\text{KG}}$

RATE HR.	KA	VAVE	$\frac{\text{W-H}}{\text{LB}}$
1	5.72	1.62	4.6
5	1.74	1.85	8.0
10	1.0	1.90	9.5

PROBLEMS

POS GRID CORROSION, DECREASE SB; Pb-CA NEG GRID

CONDUCTIVITY OF GRIDS; CJ INSERTS; AL

HEATING, +30°F; UTILIZE WASTE HEAT $E_o - E$, IR, ΔS

H_2 , SbH_3 , AsH_3 , O_2 EVOLUTION

MONITORING INSTRUMENTATION, INCLUDE REF. ELECTRODE

GENERAL PROBLEMS

MICROSCOPIC

ELECTRODE KINETICS: REDOX, RuO_2/Ti , Zn-Br_2

ZINC DEPOSITION: Zn-Br_2 , Zn-Cl_2 , ADDITIVES,
ADSORBED HYDROGEN
DENDRITE FORMATION
INCREASED LOADING 200-300 mAh/cm^2

MORPHOLOGY, LEAD ACID: PbO_2 STRUCTURE
IMPROVE UTILIZATION

TEMPERATURE DEPENDENCE OF KINETICS

CELL DESIGN

PREDICTION OF ELECTROLYTE FLOW AND MASS TRANSPORT: Zn-Br_2 , Zn-Cl_2 , REDOX

UTILIZATION OF HEAT RESULTING FROM OVERVOLTAGE, IR, ENTROPY OF CELLS

RESISTANT POLYMERS

ELECTROLYTE

PROPERTIES DATA FOR OPTIMIZATION DIFFUSIVITY, CONDUCTIVITY, TRANSFERENCE NUMBERS OF IONS, VISCOSITY

SOLUBILITY OF GASES, REAGENTS

TEMPERATURE EFFECT

SEPARATOR MATERIALS, MEMBRANES

ELECTRODES

POSITIVE GRID CORROSION

IMPROVE CURRENT DISTRIBUTION BY DESIGN

COMPOSITE GRIDS FOR INCREASED CONDUCTIVITY, FORMABILITY

SYSTEM

MONITOR CELLS, REFERENCE ELECTRODES, MICROPROCESSOR

REDOX

SRI - J. MORRILL, U.S. PAT. 3,553,017; GEL

TYPE	TEMP, °C	ENERGY DENSITY			W-H/LITER
		THEO W-H/LB	DESIGN W-H/LB	DESIGN VOL W-H/IN ³	
LEAD ACID	25	110	9	0.8	
NA/S	350	360	70	2.5	
ZN/CL ₂	50	210	70	3	
IRON REDOX	25				
CHLORIDE		31.0		1.9	115
SULFATE		14.7		0.7	42
NITRATE		21.5		1.3	78

ADVANTAGES

EXTERNAL CHARGE STORAGE
 CHEMICAL CHARGE EQUALIZATION
 HEAT TRANSFER, FLOWING ELECTROLYTE
 DRAIN TO REPLACE CELL ELEMENTS
 OPTIMIZE ELECTRODES FOR CONDUCT

PROBLEMS

NEED DESIGN DATA, ELECTROLYTE
 PARAMETERS, ELECTRODE KINETICS
 H₂ GASSING ON NEG.
 NON-UNIFORM FE DEPOSIT.

Dup

LITHIUM-METAL SULFIDE AND SODIUM-SULFUR BATTERIES
FOR SOLAR ENERGY STORAGE

by

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LITHIUM-METAL SULFIDE AND SODIUM-SULFUR BATTERIES FOR SOLAR ENERGY STORAGE

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Introduction

The incentive to consider lithium-metal sulfide and sodium-sulfur batteries for the storage of electricity generated by photovoltaic devices is in their lower projected costs (\$30 to \$45/kWhr) compared with large conventional or advanced lead-acid batteries (\$45 to \$100/kWhr).^{1,2,3} However, the lead-acid battery is at present the only battery system that can, in the near term, meet the reliability, performance, and lifetime goals necessary for the convenient storage of such energy. The application of such systems would be expected to occur in residential, shopping center, and central station power systems. It appears that the battery requirements necessary for the storage of energy from photovoltaic devices would be, to a first approximation, somewhat similar to those projected for utility load leveling.⁴ For the load-leveling application, batteries would be subjected to a daily 10-hour discharge and a 5-hour charge cycle, and would have to achieve an electrochemical energy efficiency greater than 70%, together with a lifetime of around 10 years (~ 2500 cycles) with minimal environmental impact. The probable charge/discharge cycle characteristics experienced by batteries used for the storage of solar energy can be expected to be somewhat less predictable. Considerable work is still required to solve many of the materials problems associated with both the lithium-metal sulfide and the sodium-sulfur batteries before they will be able to compete technically and economically with the lead-acid system.

The lithium-metal sulfide battery has an operating temperature of around 450°C, uses either a lithium-aluminum or lithium-silicon negative electrode, a molten salt electrolyte usually consisting of a lithium chloride/potassium chloride eutectic, and a positive electrode of either FeS or FeS₂.

The theoretical energy densities of the LiAl/FeS and LiAl/FeS₂ systems are respectively 458 and 650 Whr/kg; their current delivered energy densities

are around 15% of the theoretical values. This compares with values of around 30 Whr/kg for lead-acid batteries. To date, the FeS positive electrode has been pursued mainly for load-leveling applications where more cost-effective current collection can be performed. This is a consequence of the positive electrode being subjected to less anodic potentials than experienced with the FeS₂ electrode, particularly during cell charge. The Li/FeS₂ cell is currently being developed for electric vehicle applications where overall energy density is more important than for load-leveling applications.

For a cell of the configuration LiAl/LiCl-KCl/FeS, the discharge reaction can be represented by -

It must be appreciated that this is a gross simplification of the overall electrochemical reaction and several side reactions also occur, which can result in a loss in the overall cell capacity, particularly at the positive electrode. For example, the compound of approximate composition LiK₆Fe₂₄S₂₆Cl (known as J-Phase) can be formed in the positive electrode during electrode charge when the LiCl/KCl eutectic electrolyte is used. This material has less electrochemical reversibility than FeS and is one of the major causes of capacity loss at the positive electrode.

The unique feature of the sodium-sulfur battery is the application of the sodium ion-conducting material β-Al₂O₃ as both an effective separator and as a solid electrolyte between the sodium and sodium polysulfide active materials at the cell operating temperature of 350°C. The electrode reactions taking place in the cell are -

giving the overall reaction -

with the sodium ion migration taking place via the solid electrolyte. The theoretical energy density of the battery is 758 Wh/kg. Present work on this system emphasizes β"-Al₂O₃ where the ionic conductivity is greater than for β-Al₂O₃ due to a higher concentration of mobile sodium ions. Although having

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initial problems associated with the control of grain growth during the sintering process, the advantages of higher ionic conductivity and lower required sintering temperatures for densification have been strong motivating factors for the development of this material.

The stoichiometry Na_2S_3 indicated in Reaction 4 does not represent a true compound, but rather the composition at which Na_2S_2 separates from the sodium polysulfide melt. The cell operating temperature of 350°C is dictated both by the ionic conductivity of the sodium beta-alumina solid electrolyte and by the requirements of a liquid sodium polysulfide for the maintenance of adequate contact to the solid electrolyte.

The major technical obstacle to the commercial viability of these two systems appears to be with materials problems associated with their high temperature of operation, which results in slow degradation with time of many currently used cell components. This, together with the high anodic potentials to which the positive electrodes are subjected during cell charge, results in significant current collector corrosion problems at this electrode. Major problems are summarized in Table 1 and Table 2 for the lithium-metal sulfide and sodium-sulfur batteries, respectively.

Present Materials Problems

Lithium Sulfur

The Lithium-Aluminum Electrode⁵

This electrode, with a capacity of 0.8 Ahr/g, has shown excellent electrochemical reversibility. However, upon extended electrode cycling, the alloy morphology is found to progressively change, resulting in the formation of small alloy particles. This results both in the loss of active material utilization and in the physical loss of the alloy from the negative electrode, making the cell vulnerable to interelectrode shorting. Several approaches have been pursued to physically stabilize the alloy upon cell cycling by the synthesis of ternary alloys.⁶ However, no final answer has yet been identified.

The Lithium-Silicon Electrode⁷

Silicon can be charged to the composition Li_{15}Si where it has a capacity of 2.12 Ahr/g. Although this alloy has shown acceptable electrochemical reversibility, it has recently been observed that silicon migration into the

Table 1. SUMMARY OF PRESENT MAJOR MATERIALS PROBLEMS IN THE
LITHIUM-METAL SULFIDE BATTERY

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<u>Cell Components</u>	<u>Material Problem</u>	<u>Consequence of Material Problem</u>	<u>Approach Required to Solve Material Problem</u>
LiAl Negative	Particle size variation with time	Loss in capacity; inter- electrode shorting	Identify suitable alloy- ing agent to stabilize morphology of active material.
Li ₅ Si Negative	Silicon embrittlement of ferrous current collector	Loss in capacity; corrosion of current collector	Apply stable coatings to current collectors; identify ternary alloy for arresting Si migration.
BN Separator	High cost; questionable long-term stability	Questionable economic viability; interelectrode shorting	Identify thermodynamically stable separator materials; fabricate into convenient compounds.
Electrical Feed-Throughs	Present feedthroughs are too heavy and expensive	High cost; lower energy/ density	Identify lightweight, cost-effective feed-throughs.
FeS Positive	Formation of LiK ₆ Fe ₂₄ S ₂₆ O upon charge using LiCl- KCl	Loss in Ahr cell capacity; reduction in energy density	Modify electrolyte to minimize high K buildup next to positive before charge initiated; include additive to active mater- ial to prevent buildup of nonactive J-phase.
Positive Electrode Current Collector	Ferrous structure corrode at potentials anodic of FeS	Loss of active material containment	Apply stable coatings to current collectors; use <u>in situ</u> protection from active material.

Table 2. SUMMARY OF PRESENT MAJOR MATERIALS PROBLEMS IN THE
SODIUM-SULFUR BATTERY

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<u>Cell Component</u>	<u>Material Problem</u>	<u>Consequence of Material Problem</u>	<u>Approach Required to Solve Material Problem</u>
β'' -Al ₂ O ₃ Solid Electrolyte	Long-term slow erosion of β'' -Al ₂ O ₃ at Na/ β'' -Al ₂ O ₃ interface during charge.	Cell degradation	Identify optimum electrolyte morph- ology.
β'' -Al ₂ O ₃ Solid Electrolyte	Identify tolerable impurity levels acceptable during fabrication	Current high cost	Experimentally correlate lifetime and impurity content.
β'' -Al ₂ O ₃	Cost-effective fabrication	High cost	Compare pressing and electrophoretic forma- tion of β'' -Al ₂ O ₃ tubes.
Cell Seals	Maintenance of adequate seal between β'' -Al ₂ O ₃ ceramic and positive electrode container	Leakage of active material	Design new seal.
Positive Active Materials Container	Corrosion under anodic potential during charge	Positive container corrosion, with inverted design lower energy densities result	Apply stable coatings for positive container.
Polysulfide Cathode	High electrode polariza- tion during charge. High cost of graphite felt.	Low utilization of active material. Low voltage efficiency. High cost.	Adequately provide for polysulfide connection; identify cost-effective electron exchange site.

ferrous current collector can occur, resulting in embrittlement.⁸ Several approaches are presently being evaluated to inhibit this migration or embrittlement process, including the use of a variety of stable coatings to the current collectors and the incorporation of boron into the alloy; the latter approach has been shown to markedly reduce silicon migration.⁹ However, whether approaches currently being pursued will result in a long-term solution to this embrittlement problem has not, to this time, been conclusively determined.

Interelectrode Separation

The most widely used separator is a 2-mm thick boron nitride cloth used in conjunction with zirconia cloth. The function of this flexible separator composite is not only for the maintenance of the interelectrode spacing, but also in retainment of electroactive particles. No cell tests have yet been performed that would indicate whether this material would be stable for extended time periods. However, recent simple corrosion testing has indicated that this material may not be as stable as initially thought, particularly when in contact with unit activity lithium, a situation that can occur at the lithium-silicon negative electrode during charging in the composition range Li_4Si to Li_5Si . Present costs of this material are prohibitively high, although large-scale production may bring the cost down to an acceptable level.

FeS Positive Electrode

The Faradaic capacity that can be obtained from this electrode is typically between 60% and 70% of its theoretical value. The two predominant reasons for this are 1) inadequate current collection, and 2) the formation of the material $\text{LiK}_6\text{Fe}_{21}\text{S}_{26}\text{Cl}$, commonly called J-Phase, during electrode charge. The use of an all lithium halide ternary electrolyte (where the potassium ion is absent) circumvents this problem. However, the resulting cost penalty of such an electrolyte is unacceptable. Various additives have been included with the FeS to "break-up" the J-Phase formation, and have resulted in greater utilizations. The most widely evaluated additive has been Cu_2S , where capacities of up to 80% of theoretical in compact cells have been realized. However, this additive is largely abandoned at this time because of evidence for metallic copper formation in the boron nitride separator originating from

its addition to the positive electrode. The dimensions of the positive electrode must be carefully chosen to avoid swelling effects caused by volumetric differences that exist between charged- and discharged-state electrodes.

Positive Electrode Current Collection

The anodic potential to which the positive electrode current collector is exposed, particularly during electrode charge, make many ferrous materials susceptible to corrosion. To this time, only molybdenum has shown reasonable stability with FeS_2 , with low-carbon steels finding marginal acceptability with FeS .

Approaches that are presently being pursued for the stabilization of the positive current collectors include —

- Coatings of electronically conducting ceramic materials such as FeB , TiN , etc.
- Molybdenum coatings applied both by chemical vapor deposition and by electroplating
- Molybdenum alloys
- Boronized current collectors plus in situ protection from boron originating from the positive active material.

Sodium-Sulfur

Beta-Alumina Solid Electrolyte

An extensive amount of work has been performed on the characterization of those variables that are important to achieve a stable, high-conductivity, solid electrolyte that will be cost effective for application in the sodium-sulfur battery. Significant among these variables are —

- Electrolyte composition. Compositions varying between $\text{Na}_20.5\text{Al}_2\text{O}_3$ and $\text{Na}_20.11\text{Al}_2\text{O}_3$ have been evaluated with varying amounts of additives such as MgO or Li_2O , for the stabilization of the β "-alumina structure.^{10,11}
- Powder synthesis techniques, prior to formation into ceramic tube.
- Identification of suitable binders for obtaining "green shapes" prior to sintering.
- Tube fabrication techniques. Two general approaches are being evaluated in this area 1) isostatic pressing followed by a

sintering process, and 2) electrophoretic deposition followed by sintering. Preliminary evidence indicates that the first-mentioned technique will be the more cost-effective approach.

The interrelationship between the ceramic morphology and lifetime in the sodium-sulfur cell has not yet been clearly characterized. Although at the present time the beta-alumina ceramic does not appear to be the life-limiting component in the cell, several problems still remain. A predominant problem is the identification of those impurity levels that can be tolerated before significant deterioration in the required performance characteristics of the ceramic are compromised. This factor alone will have a major influence on the overall cost effectiveness of the sodium-sulfur battery.

A factor that may become significant during the long-term operation of this system is the nature of the ceramic surface morphology in contact with the liquid sodium negative. During charge, sodium ions reduced along grain boundaries in the polycrystalline ceramic can result in erosion of the beta-alumina. The exact mechanism of this process is still not clear, although it is probably related to local mechanical pressures produced by the sodium metal formed along the grain boundary.

Development of Effective Seals

The function of the seal in the sodium-sulfur cell is to provide effective separation between the two cell compartments containing the active materials at 350°C so that no leakage will occur, resulting in loss of either Faradaic efficiency or cell capacity. The requirements of the seal are a) to provide a hermetic barrier between cell compartments, and b) to give electrical insulation between the cell compartments.

A variety of approaches are currently being developed,^{12,13} but most approaches appear too expensive to be compatible with the cost goals set for the system. The overall seal system requires a ceramic/metal seal between the polysulfide metal container and an alpha-alumina insulator, and also a ceramic seal between the beta-alumina electrolyte and the alpha-alumina insulator. Selection of the seal system requires a design that is compatible with a ceramic beta-alumina tube that can be expected to exhibit some variation in ovality from one sample to the next.

Design of the Polysulfide Cathode

In the absence of adequate provisions for free convection of the sodium polysulfide in the cathode, significant polarization can occur at the beta-alumina/polysulfide interface during the charge phase of a cell cycle. This is caused by the local buildup of a sulfur film when the cell is operated over the composition range S and Na_2S_3 . This will result in losses not only for the overall cell capacity, but also in the voltage efficiency that can be realized from the cell. This problem can be avoided by cycling the cell over what is called the single-phase region between the compositions Na_2S_5 and Na_2S_3 . However, this approach would be unacceptable because only a theoretical energy density of 300 Whr/kg would be possible.

The electron exchange site currently used for the electrochemical reaction in the polysulfide melt is usually graphite felt. With currently projected costs at around \$10/kWhr (1975 dollars),⁴ this material may prove too expensive with substantial increases in demand not necessarily resulting in significant cost reductions.

Positive Electrode Current Collector/Container

Optimization of the energy density requires a cell design where the liquid sodium is contained within the beta-alumina tube and the polysulfide cathode is in an outer container. This outer container acts as the primary positive electrode current collector and, particularly during cell charge, is subjected to an anodic potential that has corroded many candidate materials evaluated to date. Greatest success has been found using a container fabricated from chromized 1018 steel.¹⁴ Good stability was found using this approach in cell tests lasting for one year; however, some corrosion was evident. Whether this approach will provide adequate stability for the required lifetime is as yet unknown, and requires that other material coatings also be evaluated for the maintenance of a stable polysulfide container.

Summary

The widespread terrestrial applications¹⁵ of electricity generated by photovoltaic cells will probably occur when cost goals of 50¢/Wp and installation costs of around \$1500/kWp (1975 dollars) are achieved.¹⁶ When these cost goals are met, reliable and economic approaches must be used for the storage of this electricity. At the present time, such electricity storage

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could be performed by the use of large lead-acid storage batteries where capital costs of around \$50/kWhr can be predicted. Significant cost reductions in electricity storage will occur if many of the materials problems identified in the development of the high-temperature advanced lithium-metal sulfide and sodium-sulfur batteries are solved. Close coordination will be necessary between the developers of photovoltaic devices and those involved with advanced batteries so that economic and technically viable solar collection and storage systems can be realized.

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AFS/MM/ALR

LITHIUM-METAL SULFIDE AND SODIUM-SULFUR BATTERIES
FOR SOLAR ENERGY STORAGE

Viewgraphs Presented

by

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LITHIUM ALUMINUM - IRON SULFIDE CELL

TABLE I
FREE ENERGY OF FORMATION OF SELECTED METALS
OXIDES AT 600, 700, and 800°K

FREE ENERGY OF FORMATION, - ΔG_f° (kcal/g-atm O)

COMPOUND	600°K	700°K	800°K
Y ₂ O ₃	137.71	135.42	133.14
CaO	136.72	134.28	131.85
ThO ₂	(133)	(131)	(129)
BeO	129.0	126.65	124.31
Y ₃ Al ₅ O ₁₂	-	-	-
MgO	128.19	125.62	123.06
Li ₂ O	124.82	121.47	118.12
α -Al ₂ O ₃	118.46	115.97	113.49
δ -Al ₂ O ₃	117.11	114.66	112.23
ZrO ₂	117.34	115.08	112.84
CaZrO ₃	-	-	-
TiO ₂ (Rutile)	99.66	97.49	95.33
SiO ₂	95.77	93.62	91.48

REFERENCE - JANAF THERMOCHEMICAL TABLES, 2nd EDITION. 1971.

RESISTANCE OF CERAMICS TO LITHIUM AT 400°C

CERAMIC	COMPATIBILITY			CAUSE OF FAILURE
	GOOD	FAIR	POOR	
Al ₂ O ₃			X	DISINTEGRATION
BeO			X	INTERGRANULAR DETERIORATION
BeO (HIGH PURITY)	X			
CaZrO ₃			X	CONDUCTIVE SURFACE FILM
HfO ₂			X	FRIABLE, CONDUCTIVE
LiAlO ₂			X	EXCESSIVE ATTACK
Li ₅ AlO ₄			X	EXCESSIVE ATTACK
Li ₄ SiO ₄ -Li ₃ PO ₄			X	EXCESSIVE ATTACK
MgO			X	INTERGRANULAR DETERIORATION
MgO (CRYSTAL)	X			
MgAl ₂ O ₄			X	DISINTEGRATION
SiO ₂			X	DISINTEGRATION
ThO ₂	X			
Y ₂ O ₃	X			
Y ₂ O ₃ -Al ₂ O ₃		X		
Y ₂ O ₃ -MgO		X		
ZrO ₂			X	FRIABLE, CONDUCTIVE
AlN	X			
BN (UNTREATED)			X	DETERIORATION, CONDUCTIVE SURFACE
BN (PRETREATED)	X			
SiC			X	DISINTEGRATION
SiC-AlN			X	FRAGMENTED
Si ₃ N ₄			X	INTERGRANULAR FRACTURE

MATERIALS FOR ELECTRODE CURRENT COLLECTORS

CRITERIA

- Electrical Conductivity
- Resistant to Sulfide Attack
- Resistant to Electrolyte Attack
- Low Cost
- Fabricability

STRUCTURES

- Honeycomb
- Macroporous (Retimet)
- Expanded Metal
- Protective Coatings

**FREE ENERGY OF FORMATION OF SELECTED METAL
SULFIDES AT 600, 700 AND 800°K**

Compound	Free Energy of Formation*, $-\left[\Delta G_f^0 \text{ kcal/g-atom S}\right]$		
	600°K	700°K	800°K
Ag ₂ S	15.69	15.06	14.51
CoS ₂	20.31	18.39	15.99
FeS ₂	21.50	19.14	16.80
NiS	23.92	23.34	21.40
Cu ₂ S	27.05	26.30	25.63
CoS _{0.89}	28.20	26.17	24.13
FeS	28.61	27.18	25.80
WS ₂	32.51	30.27	28.06
MoS ₂	34.54	32.32	30.12
CrS	37.36	35.78	34.21
Al ₂ S ₃	59.60	57.60	55.17
Li ₂ S	102.8	102.4	101.9

* Reference, K. C. Mills, Thermodynamic Data for Inorganic Sulphides, Selenides, and Tellurides, Butterworth & Co., Ltd., London (1974).

POTENTIALS* OF Li-Al/LiCl-KCl/M CELLS AT 450°C

Material	Potential, V	Probable Reaction
Cr	1.58	$\text{Cr}^0 \rightarrow \text{Cr}^{2+}$
Nb	2.1**	$\text{Nb}^0 \rightarrow \text{Nb}^{4+}$
Mo	2.40	$\text{Mo}^0 \rightarrow \text{Mo}^{3+}$
Mo-30W	2.4**	$\text{Mo}^0 \rightarrow \text{Mo}^{3+}$
W	3.36	$\text{Cl}^- \rightarrow \text{Cl}_2$
Fe-26Cr	1.8**	$\text{Fe}^0 \rightarrow \text{Fe}^{2+}$
Fe	1.83	$\text{Fe}^0 \rightarrow \text{Fe}^{2+}$
Cu	2.05	$\text{Cu}^0 \rightarrow \text{Cu}^+$
Ni	2.21	$\text{Ni}^0 \rightarrow \text{Ni}^{2+}$
Co	2.01	$\text{Co}^0 \rightarrow \text{Co}^{2+}$
Al	1.34	$\text{Al}^0 \rightarrow \text{Al}^{3+}$

* J. A. Plambeck, J. Chem. Eng. Data, 12 (1), 77 (1967).

** E. C. Gay et al., Proc. 8th IECEC p. 96 (1973).

FeS₂/LiCl-KCl COMPATIBILITY TEST RESULTS

MATERIAL	CORROSION RATE (μm/YR)			REMARKS AND REACTION PRODUCTS
	400°C	450°C	500°C	
MOLYBDENUM	1.4	+1.0	+16	WEAKLY ADHERENT MoS ₂ LAYER
NICKEL	2700	>6600	>6600	VERY SEVERE ATTACK; Ni ₃ S ₂ , NiS
NIOBIUM	720	2900	>4500	SEVERE ATTACK; INTERGRANULAR PENETRATION
TYPE 304 SS	3700	>6000	>6000	VERY SEVERE ATTACK; FeS, FeCr ₂ S ₄
HASTELLOY B	83	490	4000	INTERGRANULAR PENETRATION; NiS·FeS
HASTELLOY C	160	680	3200	MINOR INTERGRANULAR PENETRATION; NiS·FeS
INCONEL 617	210	1000	1700	NiS, NiCo ₂ S ₄ , Cr ₂ S ₃
INCONEL 625	380	1000	1300	PROBABLE NiS, Cr ₂ S ₃

NOMINAL COMPOSITIONS:

TYPE 304 SS (Fe-19Cr-10Ni)

HASTELLOY B (Ni-28Mo-5Fe-1Cr)

HASTELLOY C (Ni-16Mo-16Cr-5Fe-4W)

INCONEL 617 (Ni-22Cr-13Co-9Mo-1Al)

INCONEL 625 (Ni-22Cr-9Mo-4Nb-3Fe-0.4Al-0.4Ti)

FeS/LiCl-KCl COMPATIBILITY TESTS

MATERIAL	CORROSION RATE ($\mu\text{M}/\text{YR}$)			REMARKS
	400°C	450°C	500°C	
MOLYBDENUM	1.8	3.1	10	MINOR SURFACE ATTACK
NICKEL	+13	+10	+49	Fe-Ni REACTION LAYER
NIObIUM	+11	+26	+24	Fe-Nb REACTION LAYER
ARMCO IRON	440	460	410	SEVERE INTERGRANULAR ATTACK
AISI 1008	-	620	-	SEVERE INTERGRANULAR ATTACK
TYPE 304 SS	3.8	3.6	9.0	MINOR SURFACE ATTACK
HASTELLOY B	1.8	2.5	+11	COMPLEX REACTION LAYER AT 500°C
HASTELLOY C	-	0.9	+18	COMPLEX REACTION LAYER AT 500°C
INCONEL 617	0.2	2.3	+18	MINOR SURFACE ATTACK
INCONEL 625	0.9	2.7	4.9	MINOR SURFACE ATTACK
INCONEL 706	-	4.6	-	MINOR INTERGRANULAR PENETRATION
INCONEL 718	-	5.0	-	MINOR INTERGRANULAR PENETRATION
INCONEL 825	-	2.1	-	MINOR SURFACE ATTACK

CELL CORROSION OF MOLYBDENUM CURRENT COLLECTORS
IN THE POSITIVE ELECTRODE. Mo + 2S — MoS₂.

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PROTECTIVE COATINGS

TYPES OF COATINGS

- Mo

- TiN

- TiB₂

- FeB

COATING PROCEDURES

- Chemical Vapor Deposition

- Electrodeposition

- Ion Sputtering

- Vaporization

SODIUM / SULFUR CELL

LEAD-ACID

General Approaches :

- utilization of positive active material
- positive and negative electrodes - grid design and active material ratios
- positive and negative electrodes - paste formulations
- retainer - separator design
- electrolyte concentration and amount
- optimization of manufacturing processes

Specific Approaches

Globe - Union

- expander research - negative electrode
- study : any forced convection benefits?
- structural lead replacement
- modeling program - plate size and plate aspect ratio

Specific Approaches

Extra

- expanded metal positive and negative grids
- Pb-Ca-Sn positive and negative grids
- wrought alloy grid

ESB

- factorial experiments - flat plate and tubular plate, proprietary materials
- tubular innovations - thickness, retainer, multiple spines
- bipolar, pile-type battery

LEAD-ACID APPROACHES

	<u>Eltra</u>	<u>ESQ</u>	<u>Globe-Union</u>
Positive grid	Ca-Pb	Sb-Pb	Sb-Pb
Negative grid	Ca-Pb	Ca-Pb	Alloy S
Grid form	expanded mesh	cast	cast
Cell dimensions	golf car	golf car	large plates
Positive plates	flat	flat and tubular	flat

NICKEL/IRON

General Approaches :

- Redesign of positive and negative electrodes - better active material utilization
- Electrode additives to improve turn-around energy efficiency
- Manufacturing cost reductions
- Separator/barrier development - cost, resistance transport properties

Specific Approaches

Westinghouse

- Two low cost nickel electrodes using fiber metal steel grid structures
 - electrochemical impregnation
 - thermal process
- thin plate proprietary iron electrode using steel grid structure
- central electrolyte maintenance system

Specific Approaches :

Eagle-Picher

- sintered nickel electrode - increase thickness
- proprietary iron electrode - decrease thickness (1.2 Ah/cc at 25 ma/cm² and relatively insensitive to drain rate.).

APPROACH SUMMARY

	<u>Westinghouse</u>	<u>Eagle-Picher</u>
positive electrode	non-sintered, low cost	sintered, high cost
negative electrode	proprietary	proprietary
electrolyte maintenance	central (volume penalty)	local

NICKEL/ZINC

General Approaches :

- minimize zinc shape change and densification
- minimize zinc dendrite formation
- develop separator technology

Specific Approaches :

ERC

- Develop limited overcharge methods
- minimize shape change using electrode additives
- develop low cost, rolled, plastic bonded nickel electrode
- thermal management studies to handle excessive temp. rise

Specific Approaches

Could

- design studies relating plate area, power density, volumetric energy density, cycle life and cost
- NBTL test of module - 62 Wh/kg and good capacity retention
- concentrated attack - thermal management
- oxygen effect on zinc capacity
- maintenance-free cells - auxiliary electrode
- partition of zinc - proprietary approach
- concentrated but proprietary attack on other aspects involving loss of zinc capacity

Department of Energy

Division of Energy Storage Systems

Batteries

Major Program Thrusts

25%
1000's of
EV Batteries
1991-1998

65%
Commercial Super-Batteries For:
• EV's
• Disp. Solar
• Central Solar
• Util. 1995-1998

5%
Improve Industrial Processes
1985 1990
78 79 80 81 82 83 84 85 86 87 88 89 90 91 92
78-109778-14/19

Department of Energy

Division of Energy Storage Systems

Batteries

Major Missions For Battery Storage:

- Storing Solar Energy
- Powering Electric Vehicles
- Levelling Peak Demands in Electric Utility Network

Advanced Battery Development

Each System Is Currently a Candidate for Mobile and Bu Storage Needs

<u>System</u>	<u>Type</u>	<u>Contractor</u>	<u>Size of Hardware</u>
Zn/Cl ₂	—	Energy Development Associates	50 kwh Battery
Na/S	β-Alumina	Ford Motor Co.	200 wh Cells
Na/S	Glass	Dow Chemical Co.	10 wh Cells
Li/S	LiAl/F ₃ S LiAl/F ₃ S ₂	ANL w/Subcontractors	200 wh Cells

FY 78

7 %—\$11.8M

Department of Energy
Division of Energy Storage Systems

Batteries

The Electrical Vehicle Mission: The Type of Battery Required

Duty Cycle - Discharge	2-4 Hrs
 - Charge	1-6 Hrs
Energy Efficiency	50%
Life - Cycles	800 Cycles
 - Years	3-10 Yrs
Energy Density	140 kh/kg
Power Density - 15 Sec.	200 w/kg
 - Sustained	70 w/kg
Volume	200 wh/liter
Cost	\$40/kwh
Typical Size	25-40 kwh

ELECTROCHEMICAL SYSTEMS PROGRAM

BATTERY SYSTEMS : PERFORMANCE PROJECTION FOR E.V. MISSION

GOAL	LI/MS	Ford Ni/S	Dow Ni/S	Zn/Cl	Al/Air
------	-------	--------------	-------------	-------	--------

PERCENT GOAL

EFFICIENCY 50% 150 160 170 90 30

LIFE 800 cycles 100 100 100 100 100

ENERGY DENSITY 140 wh/kg 100 0 110 80 300

POWER DENSITY-15 sec 200 w/kg 100 0 150 90 60

POWER DENSITY-sustained 70 w/kg 100 0 200 90 75

VOLUME 200 cc/l 150 0 100 100 120

ISSUES — Lithium resource Safety Safety Eff, Mech. recharge

Energy Storage Systems

Advanced Batteries for EV's

Risk/Reward Relationship

Battery desirability for urban vehicles

Relative development risk

Sodium-Sulfur Battery

WHAT ARE ADVANTAGES OF THE DOW BATTERY ?

✓ HIGH SURFACE AREA

✓ LOW CURRENT DENSITY
(2 MA/CM² VS 200)

✓ HIGHEST EFFICIENCY
(90% VS 70%)

✓ VERSATILE DESIGN
(FAST CHARGE :
0.5 H VS 3 H)

✓ CHEAP, ABUNDANT
RAW MATERIALS
(\$25/KWH)

SODIUM, SULFUR, GLASS,
ALUMINUM
VS

LITHIUM, BORON NITRIDE
MOLYBDENUM, β -ALUMINA

EASE OF FABRICATION

NO LOSS OF CAPACITY
WITH AGE

ELECTROCHEMISTRY

CHLORINE STORAGE

ESSENTIAL SYSTEM SCHEMATIC

Zn/Cl₂ VEHICLE BATTERY

SIDE VIEW

ALUMINUM-AIR GALVANIC CELL (SCHEMATIC)

ELECTRIC VEHICLE SYSTEM USING AN ALUMINUM-AIR POWER CELL

TOTAL ENERGY CONVERSION EFFICIENCIES OF ALUMINUM/AIR AND SYNCRUDE TRANSPORTATION SYSTEM

Department of Energy
Division of Energy Storage Systems

Batteries

The Electric Vehicle Mission: Energy Consumption Comparison
(an example)

HYDROGEN PROBLEMS IN ELECTROCHEMICAL
AND FUEL STORAGE

by

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There are general principles of materials reliability in the presence of hydrogen which can be applied to storage systems for solar energy. These are outlined below and discussed at greater length in the attached references. In the absence of specific design information, however, only the principles and a few examples can be presented.

The first variable of importance is temperature. Classic hydrogen embrittlement occurs at ambient temperature and up to about 500 K (440°F), in most cases, while above that approximate temperature, "hydrogen attack" is of concern. The latter phenomenon has received extensive empirical study, and the results (for steels) are contained in the well-known Nelson curves. Additional work of a similar kind would probably be needed for new systems design work, although the relative simplicity of the phenomenon (hydrogen reaction with carbides, oxides, etc., to form gaseous species such as methane, followed by link-up of gas bubbles into fissures) should make laboratory materials qualification reasonably straightforward.

Additional environmental variables include operating stresses and the relative availability of hydrogen. In electrochemical environments, the local potential must be such as to permit reduction of protons (or hydronium) to hydrogen atoms at the metal surface, but this is complicated in practice because local potentials can vary considerably from place to place in a system. If hydrogen is electrochemically available, embrittlement effects tend to worsen as the driving force for its entry

increases, i.e., as gas pressures or electrochemical fugacity increase. Large values of these parameters can also lead to hydrogen precipitation at internal surfaces and the generation of high internal gas pressures, leading in turn to formation of blisters on the metal surface. Material strength and ductility are typically greatly decreased by blistering.

For hydrogen embrittlement per se, there are several materials variables of importance. These include strength level, composition, microstructure, processing history, and others. The interrelation of these is complex and is also a function of possible types of failure. For tensile overload or fatigue stresses, losses in tensile ductility are of concern, and such losses are a very general indication of hydrogen effects on mechanical properties. A much more serious problem is that of delayed failure, in which fracture occurs after a (largely unpredictable) delay time, at stresses well below the usual fracture strength. This is usually signaled by losses in strength, as well as ductility, in mechanical properties, and often occurs in materials of more complex microstructure and higher strength. A common rule of thumb for this effect is that materials of strength below about 700 MPa, or about 100 ksi, are not susceptible, and this often is true; but ductility losses may still occur and be responsible for failures of other types.

Any material to be used in a storage system (assuming hydrogen to be present and at sufficient effective pressure to be damaging) would have to be evaluated for hydrogen compatibility, either through use of literature data or (more commonly) laboratory experiments. The techniques used are well established and can be applied with confidence to determine hydrogen sensitivity, although it is not always easy to employ the resulting numbers in a design environment. Accordingly, simulations and scale-ups to design conditions are often employed as a back-up to laboratory results.

Effects may be possible to monitor in an operating system in some cases. Hydrogen attack and blistering, since they result in internal pores and fissures, should be detectable by conventional non-destructive techniques, although by the time the defects are of detectable size by current technology, the process is well advanced. Slowly-growing hydrogen cracks should also be detectable, but again, at medium and high strength levels the critical crack length is sufficiently short and the later stages of growth sufficiently rapid, as to give limited confidence in monitoring unless it can be done frequently and (hopefully) with greater sensitivity than is usually done at present.

The following list of references gives additional background in several of the areas touched on above. Most are review or overview papers.

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Specific Alloy Systems

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Applications to Operating Systems

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14. I. M. Bernstein and A. W. Thompson, "An Evaluation of Hydrogen Embrittlement Mechanisms", Mechanisms of Environment Sensitive Cracking of Materials, Metals Soc., London, 1978, p. 412.

See also Refs. 2 and 5.

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CONSTRUCTION MATERIALS FOR
BIOMASS-ENERGY SYSTEMS

by

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Biomass can be defined as "any bloomin' plant under the sun". Fortunately, obtaining energy from such a wide variety of fuels can only be accomplished in a finite number of ways. If this were not true, specifying materials of construction for equipment to be used to obtain energy from biomass could be as limitless as the list of plants which comprise it.

Before discussing biomass conversion, the subject should be clarified by listing things which are not considered to be biomass. Uranium, Thorium and Plutonium are not biomass. Coal, oil and gas are not biomass. Municipal solid-waste (MSW) and the refused-derived-fuel (RDF) which can be recovered from it by numerous processing methods are not biomass. Commercial and industrial wastes are not biomass. Human and animal digestive wastes are not biomass. Finally, dead animals, birds, fish and insects are not biomass.

Materials chosen to make equipment used to obtain energy from Uranium Thorium and Plutonium must be able to survive neutron bombardment and radiation as well as corrosion, erosion, thermal and physical stresses. Material chosen for equipment used to obtain energy from coal, oil and gas is not subjected to neutron bombardment or radiation, but it must be able to withstand fireside erosion, corrosion and thermal and physical stresses which can be orders of magnitude more severe than the conditions in a nuclear power reactor and the water side conditions can also be more severe because the cost competitive nature of fossil fuels versus electricity generated from fossil fuels can only be overcome by going to steam temperatures of 1000 degrees F. and higher and steam pressures in the range of 1800 to 2500 or more pounds per square inch.

The use of RDF as a supplementary fuel in coal fired boiler furnaces can reduce the chemical attack which occurs in the superheater sections of high pressure - high temperature boilers fired with high sulfur coal.¹ The same benefit can be achieved by the addition of elemental sulfur to raw MSW being burned in water wall incinerators producing steam at less than 800 degrees F. with furnace gas temperatures which do not exceed 1450 degrees F.²

Human and animal digestive wastes collected and transported in water require so much drying to enable them to be burned, even as a supplement to fossil fuels or in fluidized bed combustors with supplemental oil or gas fuel, that they have not been successfully used for energy production, but they can be incinerated.

No reference has been found describing energy generation using dead animals, birds, fish or insects, but it is known that they are incinerated to reduce the problems associated with burial.

Returning to the definition of biomass as "any bloomin' plant under the sun", it can be expanded by naming plant varieties that are considered to be biomass. In descending order they are: tree leaves and twigs, branches, limbs, trunks and roots; under brush and bushes; sawdust and bark; corn stalks, corn cobs, corn stover and even seed corn that has been chemically treated and stored too long³; vines, seed pod hulls and the discarded plants they were removed from; sugar cane, sorghum plants, bamboo, cattails, reeds, water hyacinths, fresh water weeds, algae, kelp and seaweeds.

Energy in the form of heat can be obtained from all biomass by complete combustion, when the material has been dried. Solid, liquid or gaseous secondary energy sources may be produced from biomass by incomplete combustion (pyrolysis), anaerobic digestion or fermentation (biogasification) and acid or enzyme hydrolysis of cellulosic materials. Tertiary energy sources may be obtained by further processing of some secondary energy source materials using condensation, chemical conversion and fermentation.

Complete combustion of biomass must be preceded by preparation that can consume significant amounts of energy. If air drying is used, excess handling of the material into and out of carefully designed drying piles is required. If heat drying is used, fuel is required and the system's efficiency is reduced.

Complete combustion of biomass in the boiler of a large (600-1200 MW) fossil fuel fired electricity generating unit's boiler furnace would require the development of new material handling equipment for the logs, branches and scrap to feed them into chippers which would have to be designed, developed and demonstrated to be as reliable as the unit's other power generating equipment. Conveyors, bunkers, feeders, burners, grates, soot blowers, ash hoppers, ash conveyors, fly ash collectors, storage hoppers and conveying systems would all have to be redesigned.

The problems associated with complete combustion for power generation are such that conversion of existing coal, oil or gas fired unit's boilers and auxiliary systems and retraining of the operators would be prohibitively costly. The design fabrication erection and start-up of the new fuel handling

system, the new burners and the new ash handling system would present so many problems ⁴ that it should be attempted only when all else fails.

Collecting, preparing and firing biomass as a supplementary fuel for a coal fired boiler is the most attractive method of accomplishing its complete combustion. It should only be used in cyclone fired or moving grate boiler furnaces. Firing prepared biomass as a supplementary fuel in a powdered coal fired boiler furnace should not be attempted until new types of wood shredders are available which will cut the biomass into such small pieces they will move down through the furnace flames at the same rate as the powdered coal, and combustion will have been completed by the time they enter the ash pit.

Complete combustion of biomass in industrial and heating boiler furnaces should be easier to accomplish because of their smaller sizes and lower steam pressure and temperature requirements. However, even though the design and building of the biomass fuel gathering, transport, storage, preparation and firing system, the boiler and its furnace and the ash gathering and handling systems have been carefully done; testing and operator training have been thorough and operating experience is satisfactory, it all could have been done easier with gas.

Fuel gas is the ideal fuel, and natural gas, methane or (SNG) is its ideal form. Biogasification by anaerobic digestion of wood free biomass with animal or human digestive wastes will produce gas which can be readily treated to remove moisture, carbon dioxide and minor amounts of hydrogen sulfide to form methane or (SNG) ⁵, having a heat content that is approximately 1000 BTU/SCF. This fuel gas may be used in all types of boilers and heating equipment and in gas turbines and reciprocating engines.

Pyrolysis, using oxygen for combustion (Union Carbide Co.'s "Purox System") of prepared biomass, including wood, will produce a lower heating value (250-300 BTU/SCF) fuel gas. This gas may be used in all types of boilers and heating equipment, in gas turbines and in reciprocating engines.

Pyrolysis, using air for combustion (Carborundum's "Torrax System") of prepared biomass, including wood, will produce a still lower heating value (140-180 BTU/SCF) fuel gas. This gas may be used in many types of boilers and heating equipment. It can be used more efficiently if the hot gases leaving the pyrolizer enter the furnace in which they are to be burned without being cooled. Used in this way, the gas carries with it the volatilized tars and fine incompletely burned particulates, and the products of combustion are more completely used for heating.

Liquid fuels may be made from the cellulosic materials in biomass by solvent pretreatment to prepare it for hydrolysis to sugars by either acids or enzymes. The sugars can then be changed to ethanol by fermentation.⁶ The ethanol produced by this process is a clean burning fuel. It can be added to gasoline. It can be changed into gasoline by further processing. It can also be converted to ethylene by reprocessing. As petroleum supplies dry up and the price of oil and natural gas continues to increase, the market for ethanol produced from biomass, using the "Purdue Process"⁶, will become a significant factor in the U.S. economy. Some of the near future uses that are mentioned by M. R. Ladisch⁶ are:

1. Industrial Alcohols and Liquid Fuels.
2. Chemical Feedstocks.

3. Microbial Polysaccharides.

4. Protein Supplements.

Preparation of this rapid survey of the presently available methods of producing energy from biomass has been enjoyable because it provides optimism and confidence in the future for the energy dependent economy and well being of the people of the United States and other countries. This was a relief from the "Doom and Gloom" syndrome which has infected the media and governmental regulators because of fears for our health and environment if nuclear fuel and coal become the basic energy sources as oil and gas prices increase due to their depletion at home and abroad.

Optimism for the future has been reinforced by study of the energy conversion methods examined to find out what special materials of construction will be required. No new and exotic alloys or super metals will be needed. Carbon steels, low alloy steels, stainless steels and ceramic materials which are commercially available today will serve very well for energy production from biomass in the future by the methods and systems discussed.

Complete, direct burning of biomass as a fuel for steam generation and direct heating throughout the entire range from power generation to home heating can be carried out well, and equipment life similar to that being experienced with fossil fuels today can be expected. The same conclusions apply to the use of biomass as a supplement to coal.

The major deficiency found are the problems being experienced with presently available size reduction equipment such as choopers, chippers and hammer mills. They all appear to wear too rapidly, break too often and require too much power.

Pyrolytic gasification of biomass using Purox, Torrax and other presently available gasifiers has been demonstrated to be possible in ceramic lined vertical and horizontal heating chambers. Again, today's metals and ceramics can be used and the processes have not developed any surprises for the designers or operators. Preparation equipment and economics are the two apparent problem areas.

Biogasification by anaerobic digestion makes the least demands on metallurgists of any of the processes studied. References ranging from "Methane; The Fuel of the Future" by Bell, Boulter, Dunlop and Keiller, published in 1973, and "Methane Digesters for Fuel Gas and Fertilizer", published by the New Alchemy Institute, also in 1973, to "Anaerobic Digestion: The Rate Limiting Process and the Nature of Inhibition" by Finney and Evans, printed in Science, Vol. 190, in 1975, "Make SNG From Waste and Biomass" by D. L. Klass, printed in Hydrocarbon Processing in April of 1976, and "Farm-Scale Generation of Bio-Gas" by Goodrich, Gustafson and Hauer, presented at the 1978 Midwest Energy Conference in November, in Chicago, were studied and the Hammond, Indiana Sanitary District, Anaerobic Digestion Sewage Plant was visited to confirm conclusions that no exotic materials are needed. Cast iron, plain carbon steel, concrete, glass fibre reinforced plastics, 55 gallon steel drums and black iron pipe all seem to work well. The most interesting materials were found in the laboratory of the Hammond plant, but again, similar materials can be found working well in many modern chemical laboratories.

The "Purdue Process" described in reference (6) can all be performed in systems made of type 304 stainless steel. Discussion with one of the authors brought out that use of neutral pH rather than the present acid (pH 2-4) solutions is being examined, and if it can be accomplished, the capital cost of the equipment can be reduced by changing the material of construction to carbon steel. Discussion with an engineer working for American Maize which produces sugars for human consumption developed the fact that their processes are carried out in type 316 stainless steel piping and equipment because their product materials are treated with sulfur to control damaging bacteria.

In conclusion, it may be said that using biomass as an energy source will require no new materials of construction; it can be done quite well with intelligently chosen, presently available products for which significant information is now available.

APPENDIX 1 - REFERENCES

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MATERIALS ENVIRONMENT IN CONTINUOUS
SULFURIC ACID HYDROLYSIS OF CELLULOSIC MATERIALS

by

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The acid hydrolysis of cellulosic materials has been examined both as a profitable means of refuse disposal and, more recently, as an economical source of a fuel, namely, ethanol. Preliminary plant designs based on bench scale experiments carried out at the Thayer School predicted ethanol prices competitive with current values. In order to provide an understanding of the environment encountered by the materials of construction, this paper will present an overview of a continuous flow hydrolysis system and then describe the existing bench scale system and the proposed plant designs. The glucose fermentation will not be discussed, as it involves standard industrial practice.

1. THE ACID HYDROLYSIS OF CELLULOSIC MATERIALS

There are three essential characteristics of the hydrolysis reactor discussed here: it is a continuous, isothermal, plug flow reactor. Each of these characteristics is a function of the nature of acid hydrolysis, so it is useful to start with a brief summary of the important chemical aspects.

The cellulosic materials being considered as hydrolysis feedstocks consist of cellulose, hemicellulose and lignin. Though the proportions vary with the specific substrate, cellulose is the major component. Present in both crystalline and amorphous forms, it is a glucan, or a polymer of anhydroglucose units. Hemicellulose contains a mixture of hexans and pentosans, predominantly glucan and xylan. Lignin is a noncarbohydrate polymer which remains essentially insoluble in acid solution.

On a general basis, the acid hydrolysis of a cellulosic material proceeds as follows: The crystalline cellulose fraction is hydrolyzed to glucose, which in turn forms by-products:

crystalline cellulose $\rightarrow$ glucose $\rightarrow$ decomposition products.

At the conditions necessary to hydrolyze the crystalline fraction, the reactions of the amorphous fraction and of the hemicellulose are virtually instantaneous. Therefore, in our analysis of the kinetics, these components are considered to be initial concentrations of glucose and xylose:

amorphous cellulose : glucose $\rightarrow$ decomposition products

hemicellulose : xylose $\rightarrow$ decomposition products

Since the formation of by-products proceeds readily at the conditions necessary to hydrolyze crystalline cellulose, the objective is to maximize the

selectivity; that is, the ratio of the rate of glucose formation to the rate of glucose decomposition. Two approaches have traditionally been used: low temperature, concentrated acid and high temperature, dilute acid. The relatively long reaction time for the low temperature processes requires a relatively large investment in plant equipment for a given glucose production. This capital cost and the material costs involved in using and neutralizing concentrated acid seem to have precluded commercial success.¹ Alternatively, the high temperature approach, with a shorter reaction time, is well suited to a continuous process. Less reactor volume is required for the same output, and acid and neutralization costs are lower. These advantages provide the basic motivation for the continuous flow reactor.

Although the hydrolysis of a cellulosic material in dilute acid is a heterogeneous reaction, it can be modeled as a series of consecutive, homogeneous first-order reactions. The kinetic model can then be used to determine the optimum conditions for the maximum glucose yield. Figures 1 and 2 show the dependence of the yield on residence time for various temperatures and acid concentrations. It is apparent that the maximum yield increases with temperature, so it is desirable to operate isothermally, at a high temperature. This is the second characteristic of the continuous flow reactor. Ideally, the process would operate with instant heating and cooling times. However, at higher temperatures, the short reaction times of one or two seconds are of the same order as the heating and quenching time, so that the total reaction would not be isothermal. This limits the maximum practical temperature to about 240°C.

In order to maintain an optimum yield, the residence time dispersion of the process stream must be limited. In other words, all elements of the flow should have the same velocity. This defines the third characteristic of the reactor -- a flat velocity profile, or plug flow. Although a Newtonian fluid has a parabolic velocity profile, the thixotropic nature of a cellulosic slurry allows the plug flow concept to be approached in practice. For those cases in which this does not happen, the use of in-line static mixers is contemplated.

FIGURE 1

FIGURE 2

2. BENCH SCALE SYSTEM

A laboratory scale system has been designed and operated at Dartmouth using the concepts outlined above. The two primary objectives of the research presently underway are to demonstrate the viability of a continuous, plug flow reactor under the conditions of commercial interest, and to evaluate the kinetic parameters for various cellulosic substrates. The flowsheet for the existing system is shown in Figure 3. Typical operating conditions are 500 - 600 psig, 190 - 240°C, 1/2 to 2% sulfuric acid (on the aqueous phase), and 5 to 15% solids. Flow rates are on the order of 250 - 300 ml/min, and the residence time in the reactor section is 12-1/4 seconds. In this configuration, a slurry of corn stover, for example, is heated electrically through the pipe wall to the desired temperature and then injected with concentrated (60 - 98%) sulfuric acid. The acid is introduced in a turbulent mixing tee to ensure rapid initiation of the reaction. All tubing is 1/4", .035" wall except the reactor section, which is 1/2", .089" wall, and the heat exchanger which is a .027" ID glass-lined capillary tube contained in a 1/2" shell. Materials of construction are SS 316 before acid injection, and Carpenter 20Cb-3 after.

Operating experience over the past sixteen months has shown the major materials problem to be corrosion of the acid mixing tee. The severe corrosion occurs with the combination of high temperature and the dilution of the acid. The dilution aspect is important because the nature of the corrosion changes from oxidizing to reducing as the acid is diluted. To protect the dilution section of the mixing tee, machinable ceramic sleeves have been inserted. The ceramic has shown no measurable corrosion in a year's use -- about 100 hours' service. The reactor section also exhibits significant corrosion. A length of Carpenter 20Cb-3 tubing used in an earlier design was severely attacked in a 5% acid environment. The corrosion rate for about 50 hours' service exceeded 500 mpy.

Currently, the system is being modified to incorporate direct steam injection heating, which will both eliminate the need for high temperature acid injection and increase the heating capacity. Additionally, the reaction will be quenched by flash cooling of the hydrolyzate in place of the heat exchanger.

Figure 3

From: Thompson, David R., "Acid Hydrolysis as a Means of Converting Municipal Refuse to Ethanol: Process Kinetics and Preliminary Plant Design", Master of Engineering Thesis, Thayer School of Engineering, Hanover, N.H., 1977

3. PLANT DESIGNS

On the basis of the engineering and kinetic data collected in operation of bench scale hydrolysis systems, several plant designs have been proposed.³ The flowsheets for two such designs are included here (Figures 4 and 5). The first design hydrolyzes 885 tons per day of newsprint at 500 psig, 230°C, and 1% acid. The feed is pulped and dewatered to 40% solids using routine paper pulp processing equipment. The slurry and 50% sulfuric acid are fed to the reactor by a screw pump. Rapid heating is accomplished with live steam addition. The nominal slurry concentration in the reactor is 30% solids, and the residence time is 0.19 minutes or 11.4 seconds. The hydrolyzate is flashed to 134°C and 30 psig to quench the reaction. Furfural, a valued by-product, is recovered from the flash vapor, and the liquid is transferred to a continuous stirred tank neutralizer. The lime neutralization is performed at 134°C to minimize the solubility of calcium sulfate. The lignin, residual cellulose and calcium sulfate are collected in a centrifuge and fed to a boiler for process power and heat. Materials of construction are stainless steels as listed in Table 1, except for the neutralization apparatus, which is carbon steel. In the design, Carpenter 20Cb-3 was used for the reactor section. At present, this appears to be an unsuitable material, and the final choice still requires attention. It is worthwhile to note that the reactor and screw pump account for only 3% of the equipment cost, so that a more expensive material will not have a major impact on the process economics.

The second design utilizes essentially the same flowsheet as the first, but is based on a 10% slurry concentration. The major differences are the absence of the V-cone press, the use of slurry preheat, and the addition of an evaporator to concentrate the glucose solution to 10% for economical fermentation. The energy requirements of this design are higher, so that only the steam demand is met by incineration of the centrifuge cake. Commercial electricity is purchased to meet the power requirements.

CONCLUSIONS

Perhaps the most important materials consideration is the choice of acid. Hydrochloric and sulfurous, as well as sulfuric, acid are candidates which should be considered in materials analyses.

FIG. 4 PROCESS FLOW SHEET FOR ACID HYDROLYSIS. DESIGN I 30% SLURRY. MATERIAL FLOW IN (TONS/DAY)³

From: Grethlein, Hans E., "Comparison of the Economics of Acid and Enzymatic Hydrolysis of Newsprint"; Biotechnology and Bioengineering, Vol. XX, 1978

FIG. 5 PROCESS FLOW SHEET FOR ACID HYDROLYSIS, DESIGN II 10% SLURRY. MATERIAL FLOW IN (TONS/DAY)³

From: Grethlein, Hans E., "Comparison of the Economics of Acid and Enzymatic Hydrolysis of Newsprint", Biotechnology and Bioengineering, Vol. XX, 1978

Table 1. CAPITAL EQUIPMENT FOR ACID HYDROLYSIS OF NEWSPRINT
Design 1: 30% Slurry, Plant Capacity 885 ton/day

PROCESS EQUIPMENT			No. of Units
Item	Unit Specification		
<u>Feed Preparation</u>			
Conveyor		2	
Pulper and drive motor	22 ft diam, s.s. tank 500 hp	2	
Stock chest with agitators	500,000 gal, two 75 hp agitators	1	
Stock pumps and motors	2000 gal/min with 100 hp	2	
Liquid cyclones	30 in. diam	2	
Dewatering screws	15 hp per screw, 304 s.s. contact parts	12	
V-cone presses	150 ton/day dry pulper press and 70 hp 305 s.s. contact parts	6	
<u>Reactor Section</u>			
Acid feed pump and motor	5 gal/min, 1 hp	2	
Reactor screw feeder and motor	100 hp Carpenter 20	2	
Plug flow reactor and heater	1½ diam x 46 ft Carpenter 20	2	
Flash tank	5 ft diam, 2000 gal clad s.s.	1	
Flash liquid pump and motor	25 hp	2	
Neutralizing tank with agitator	11,000 gal, 20 hp carbon steel	1	
Lime slurry pump and motor	10 hp	2	
Lime storage tank with agitator	55,000 gal, 50 hp carbon steel	1	
Hydrolyzate pump and motor	10 hp, 900 gal/min	2	
Centrifuge	30 in. diam x 20 in., 100 hp, s.s.	2	
Heat exchanger	8000 ft ² carbon steel	1	
Hydrolyzate tank	2,000,000 gal carbon steel	1	

From: Grethlein, Hans E., "Comparison of the Economics of Acid and Enzymatic Hydrolysis of Newsprint", Biotechnology and Bioengineering, Vol. XX, 1978

Table 2. CAPITAL EQUIPMENT FOR ACID HYDROLYSIS OF NEWSPRINT
Design #2: 10% Slurry, Plant Capacity 885 ton/day

PROCESS EQUIPMENT		
Item	Unit Specification	No. of Units
<u>Feed Preparation</u>		
Conveyor		2
Pulper and drive motor	22 ft diam, s.s. tank 500 hp	2
Stock chest with agitator	500,000 gal, two 75 agitators	1
Stock pumps and motors	2000 gal/min, 100 hp	2
Liquid cyclone	30 in. diam	2
Dewatering screws	15 hp per screw, 304 s.s. contact parts	12
<u>Reactor Section</u>		
Preheater feed pump with motor	1200 gal/min, 60 hp	2
Preheaters	4500 ft ² , 304 s.s.	3
Reactor feed pump with motors	400 gal/min, 180 hp Carpenter 20	4
Acid pump with motor	18 gal/min, 8 hp	2
Plug flow reactor	1 ft. diam x 35 ft. Carpenter 20	4
Flash tank	4600 gal, clad s.s.	1
Flash liquid pump with motor	22 gal/min	2
Neutralizer tank with agitator	15,000 gal, 40 hp carbon steel	1
Lime slurry pump with motor	30 gal/min, 1 hp	2
Lime storage tank with agitator	55,000 gal, 50 hp, 30% slurry	1
Hydrolyzate pump with motor	1200 gal/min, 10 hp	2
Centrifuge	30 in. diam x 30 in., 200 hp s.s.	2
Hydrolyzate tank	2,000,000 gal, carbon steel	1
Heat exchanger	304 s.s.	1
<u>Evaporation Section</u>		
	long vertical tube carbon steel	
	5 effects with total surface area of 65,000 ft ²	

From: Grethlein, Hans E., "Comparison of the Economics of Acid and Enzymatic
Hydrolysis of Newsprint", Biotechnology and Bioengineering, Vol. XX, 1978

One potentially serious corrosion problem is the flash cooling of the hydrolyzate. The orifice used in this operation would be exposed to a high velocity, flashing flow containing solid particles and acid. The choice of material for such a device is somewhat difficult, as the extent of readily available corrosion data for conditions of high temperature and pressure is limited. It is planned to include a corrosion testing section in the system currently under development. Possible configurations include the use of orifice plate or sleeve type inserts in the reactor section.

The plant designs presented here are preliminary, so some significant changes in future designs should be expected. Though the process configuration could be significantly altered, it is unlikely that the reaction conditions would become more severe.

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OPERATION OF THE
BIOMASS LIQUEFACTION FACILITY
ALBANY, OREGON

by

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BACKGROUND

BIOMASS LIQUEFACTION HAS BEEN AROUND FOR A LONG TIME IF WE CONSIDER THAT THE TAR RESULTING WHEN CHARCOAL IS MADE BY BURNING WOOD IN AN OXYGEN DEFICIENT ENVIRONMENT IS LIQUID BIOMASS. EARLY IN THIS CENTURY, BERGIUS STUDIED THERMAL DECOMPOSITION AND HYDROGENATION OF CELLULOSE, PRODUCING SMALL QUANTITIES OF OIL RESEMBLING PETROLEUM.

IN THE EARLY 1930'S, HYDROGENATION OF SAWDUST AND COTTON IN TETRALIN MEDIUM, RESULTING IN FORMATION OF LIQUID WAS REPORTED IN THE CANADIAN JOURNAL OF RESEARCH. VARIOUS OTHER INVESTIGATORS PERFORMED RELATED STUDIES ABOUT THAT TIME.

THE DEPARTMENT OF ENERGY AND ITS PREDECESSOR ORGANIZATION, THE ENERGY RESEARCH DEVELOPMENT ADMINISTRATION (ERDA), AND THE PITTSBURGH ENERGY RESEARCH CENTER (PERC), WHICH IS PART OF THE UNITED STATES BUREAU OF MINES (USBM), EARLY RECOGNIZED THE IMPORTANCE OF DEVELOPING ALTERNATE FUELS AND ENERGY SYSTEMS. THUS BEGAN SERIOUS EFFORTS TO CONVERT BIOMASS TO A LIQUID FUEL. LABORATORY RESEARCH WAS CARRIED OUT AT THE PERC BEGINNING IN THE LATE 1960'S. THESE BENCH-SCALE INVESTIGATIONS, CARRIED ON INTO THE EARLY 1970'S, SOON SHOWED THE POTENTIAL FOR PRODUCING A SYNTHETIC CRUDE OIL FROM CELLULOSIC WASTES, INCLUDING SUCH MATERIALS AS WOOD, URBAN REFUSE, AGRICULTURAL WASTES (CORN COBS, MANURE), AND OTHER ORGANIC WASTES.

WITH THE TECHNICAL POSSIBILITY ESTABLISHED, A PRE-LIMINARY ECONOMIC FEASIBILITY STUDY WAS CONDUCTED FOR THE BUREAU OF MINES.

FOLLOWING THE ENCOURAGING RESULTS OF THIS STUDY, THE USBM COMMISSIONED THE RUST ENGINEERING COMPANY TO DESIGN A PILOT PLANT TO PROCESS UP TO THREE TONS PER DAY OF WOOD CHIPS. THIS PILOT PLANT WAS INTENDED TO BE EQUIPPED WITH COMMERCIALY AVAILABLE COMPONENTS.

FURTHER STUDIES CONFIRMED THE DESIRABILITY OF TESTING THE PROCESS IN THE PILOT PLANT. UNDER CONTRACT TO USBM AND ITS SUCCESSOR ORGANIZATION, ERDA, THE PILOT PLANT WAS CONSTRUCTED BY MAECON, INC., IN ALBANY, OREGON AT THE BUREAU OF MINES METALLURGICAL RESEARCH CENTER (SLIDE 1). RUST HAD NO ROLE IN EITHER FINAL EQUIPMENT SELECTION OR CONSTRUCTION SUPERVISION DURING THIS PHASE OF WORK.

FROM JANUARY, 1976 TO JUNE 1978, THE ALBANY PILOT PLANT WAS OPERATED BY BECHTEL CORPORATION PURSUANT TO THE OVERALL OBJECTIVE OF THE DOE'S PROGRAM TO OBTAIN DEFINITIVE PROCESS INFORMATION TO PERMIT COMMERCIAL DESIGN OF A PLANT FOR CONVERSION OF BIOMASS TO SYNTHETIC CRUDE OIL.

ALTHOUGH THERE HAVE BEEN MECHANICAL AND OPERATING PROBLEMS, AS IS OFTEN THE CASE WITH SMALL FIRST STAGE PILOT PLANTS, THE PROCESS HAS SHOWN SUFFICIENT PROMISE FOR THE DOE TO CONTINUE THE PILOT PLANT ACTIVITY FOR AN ADDITIONAL TWO-YEAR OPERATIONAL PERIOD. WHEELABRATOR CLEANFUEL CORPORATION, WITH THE RUST ENGINEERING COMPANY RESPONSIBLE FOR OPERATION, WAS AWARDED THE CONTRACT FOR THIS PERIOD.

THE SIGNIFICANCE OF THE PROJECT AND THE CONSIDERABLE INTEREST THAT HAS BEEN EVIDENCED IN THE PILOT PLANT. IN THE RECENT PAST IS READILY UNDERSTOOD WHEN IT IS CONSIDERED THAT THE NATION'S THREE BILLION TONS PER YEAR OF SOLID ORGANIC WASTE COULD YIELD SOME ONE AND ONE-HALF BILLION BARRELS OF OIL ANNUALLY IF ONLY HALF OF THIS WASTE WERE PROCESSED IN LIQUEFACTION PLANTS.

THOSE INTERESTED IN SOLAR ENERGY WOULD NATURALLY CONSIDER THE POSSIBILITY OF CULTIVATING FAST GROWING CROPS TO SUPPLY THE BIOMASS ON A LARGE SCALE TO SERVE AS FEEDSTOCK FOR A LARGE COMMERCIAL PLANT OF 2000, OR MORE, TONS PER DAY.

THE OIL RESULTING FROM THE PROCESS IS LOW IN SULFUR, SUITABLE FOR USE IN POWER PLANTS OR AS FEEDSTOCK FOR CONVERSION TO GASOLINE AND DIESEL FUELS. LABORATORY PRODUCED SAMPLES SHOW THE FOLLOWING PROPERTIES:

SPECIFIC GRAVITY	1.1
VISCOSITY, CP (140°F)	515
HEATING VALUE, BTU PER POUND	15,000
COMPOSITION, % CARBON	76.62
HYDROGEN	7.05
NITROGEN	0.13
SULFUR	0.14
OXYGEN	20.05

POSSIBLY EVEN MORE IMPORTANT ECONOMICALLY THAN FUEL ARE THE POTENTIAL APPLICATIONS AS PROCESS FEEDSTOCKS.

THE PROCESS CAN BE REDUCED TO TWO BASIC EQUATIONS WHICH INVOLVE REACTING CARBON MONOXIDE AND HYDROGEN WITH WOOD WASTES (OR OTHER CELLULOSIC AND LIGIN MATERIALS) IN THE PRESENCE OF SODIUM CARBONATE AS A CATALYST AT TEMPERATURES UP TO 700°F AND PRESSURES UP TO 4000 PSIG. CARBON MONOXIDE REACTS WITH SODIUM CARBONATE IN THE PRESENCE OF WATER TO FORM SODIUM FORMATE WHICH, IN TURN, REACTS WITH CELLULOSE IN THE WOOD WASTES TO FORM OIL AND REGENERATE SODIUM CARBONATE. THE FOLLOWING REACTIONS ARE BELIEVED TO BE TYPICAL:

THE ACCOMPLISHMENT OF THE APPARENTLY SIMPLE DEOXY-GENATION REACTION, HOWEVER, IN THE BIOMASS LIQUEFACTION PILOT PLANT, INVOLVES SEVERAL UNIT OPERATIONS FUNCTIONING IN SOMEWHAT DIFFICULT CONDITIONS BECAUSE OF CONSTRAINTS SUCH AS TEMPERATURE, PRESSURE, SMALL SIZE AND THE DESIRE FOR COMMERCIAL AVAILABILITY FOR ALL ITEMS OF EQUIPMENT. THE SIMPLIFIED FLOW DIAGRAM FOR THE PROCESS IS SHOWN IN SLIDE 2. IN ITS SIMPLEST TERMS, THE PRIMARY OPERATING MODE CONSISTS OF:

- * DRYING THE BIOMASS (WOOD IN OUR PILOT PLANT) TO 4% MOISTURE.
- * GRINDING TO 50 MESH POWDER.
- * SLURRYING THE WOOD POWDER WITH CARRIER VEHICLE OIL.
- * INJECTION INTO THE HEATED REACTOR AT PRESSURES UP TO 4000 PSIG AND TEMPERATURES UP TO 700°F.

- * PRESSURE LETDOWN.
- * SEPARATION OF SOLIDS (CATALYST AND UNREACTED WOOD) FROM THE OIL.

PROCESS AND EQUIPMENT DETAILS

THE BIOMASS FEEDSTOCK IN PRESENT USE IS DOUGLAS FIR WOOD CHIPS PURCHASED FROM A NEARBY PAPER MILL. THESE CHIPS ARE STORED IN AN OPEN SHED (SLIDE 3). THEY ARE MOVED BY A FRONT END LOADER TO THE FEED CONVEYOR FOR TRANSFER TO THE DRYER FEED STORAGE BIN (SLIDE 4).

THE WOOD CHIPS ARE WITHDRAWN FROM THE STORAGE BIN BY A CONTROLLED RATE TABLE FEEDER TO A GAS FIRED ROTARY DRYER WHERE MOISTURE CONTENT IS REDUCED FROM ABOUT 55% TO 4% MAXIMUM USING HOT COMBUSTION PRODUCTS FOR HEATING (SLIDE 5). THE DRIED CHIPS THEN FEED TO A HAMMER MILL GRINDER AND ARE THEN SCREENED TO 50 MESH SIZE (SLIDE 6).

THE DRIED WOOD, AS WELL AS THE GRINDING AND SUBSEQUENT WOOD PROCESSING OPERATIONS, ARE KEPT IN A NITROGEN ATMOSPHERE TO MINIMIZE MOISTURE PICK-UP AND EXPLOSION HAZARD.

THE WOOD POWDER IS CONVEYED PNEUMATICALLY TO AN ELEVATED FEED BIN IN A CLOSED SYSTEM USING NITROGEN AS THE CONVEYING MEDIUM (SLIDE 7).

THE CATALYST, SODIUM CARBONATE, IS PREPARED AS A 20% AQUEOUS SOLUTION FOR INJECTION INTO THE REACTION SYSTEM BY MEANS OF A CONVENTIONAL HIGH PRESSURE METERING PUMP.

CARBON MONOXIDE AND HYDROGEN IS RECEIVED AS GAS IN STANDARD OVER-THE-ROAD TUBE TRAILERS. THE CARBON MONOXIDE

MIXED WITH GASEOUS HYDROGEN IS COMPRESSED TO REACTION PRESSURE IN A NON-LUBRICATED, NON-CONTAMINATING DIAPHRAGM-TYPE COMPRESSOR. THE GASEOUS MIXTURE IS FED CONTINUOUSLY INTO THE SYSTEM EITHER AT THE PREHEATER OR THE REACTOR (SLIDE 8).

WOOD POWDER IS CONTINUOUSLY FED FROM THE WOOD SURGE BIN THROUGH A WEIGH FEEDER TO THE WOOD-OIL BLENDER (SLIDE 9).

ANTHRACENE OIL IS PRESENTLY USED AS A CARRIER VEHICLE. IT IS PUMPED FROM THE OIL FEED TANK TO THE WOOD-OIL BLENDER, WHERE IT IS MIXED WITH WOOD POWDER IN A CONE SHAPED BLENDER WITH HELICAL SCREWS ON ROTATING ARMS THAT SWEEP THE SIDE WALLS.

THE WOOD-OIL SLURRY FROM THE BLENDER, AT 25 TO 30% WOOD CONTENT, IS PUMPED INTO THE REACTOR THROUGH A FEED SLURRY CIRCULATING PUMP AND A HIGH PRESSURE FEED SLURRY PUMP; THENCE THROUGH AN ELECTRICALLY HEATED SCRAPED SURFACE FEED PREHEATER TO AN ELECTRICALLY HEATED REACTOR, WHERE TEMPERATURE AND PRESSURE ARE MAINTAINED AND REACTION TIME OCCURS.

CATALYST SOLUTION AND A GASEOUS CARBON MONOXIDE-HYDROGEN BLEND ARE INJECTED EITHER AHEAD OF THE PREHEATER OR DIRECTLY INTO THE REACTOR.

HIGH PRESSURE AND HIGH TEMPERATURE EQUIPMENT ARE CONSTRUCTED OF TYPE 316 STAINLESS STEEL. THE SLURRY CIRCULATING PUMP IS A MOYNO RESILIENT STATOR TYPE WHILE THE HIGH PRESSURE SLURRY FEED PUMP IS A BRAN AND LUBBE VARIABLE STROKE POSITIVE DISPLACEMENT TYPE WITH BALL CHECK VALVES. SPECIFIC OPERATING PROBLEMS RELATING TO MATERIALS OF CONSTRUCTION WILL BE DISCUSSED LATER.

THE REACTOR EFFLUENT IS COOLED IN AN AIR COOLED HEAT

EXCHANGER PRIOR TO PRESSURE LETDOWN WHERE WATER AND LIGHT OILS FLASH AND ARE SEPARATED IN A LOW PRESSURE FLASH SYSTEM. COOLING THE VENTED GAS PERMITS THE RECOVERY OF LIGHT OILS AND WATER. VENTED GAS AND NON-CONDENSIBLES ARE INCINERATED.

AS DESIGNED, A CENTRIFUGE WAS INTENDED TO SEPARATE THE PRODUCT OIL FROM ANY SLUDGE OF CATALYST AND UNREACTED WOOD, SINCE BENCHSCALE BATCH EXPERIMENTS HAD SHOWN THIS SEPARATION POSSIBLE. TO DATE, NO PRODUCT HAS BEEN SUCCESSFULLY CLARIFIED BY THE CENTRIFUGE DUE TO HIGH VISCOSITY OF THE OIL MIXTURE.

THE PROCESS, AS WE HAVE JUST REVIEWED, FEEDS A SLURRY OF 30% BIOMASS IN 70% VEHICLE OIL, THE MAXIMUM THAT COULD BE PUMPED WITH COMMERCIAL EQUIPMENT WHEN THE DETAILED DESIGN ENGINEERING WAS UNDERTAKEN IN 1973. THIS MEANS THAT 70% OF THE CIRCULATING LOAD IS PUMPED, HEATED, AND COOLED, ACTING ONLY AS AN INERT CARRIER, A WASTE OF CONSIDERABLE ENERGY THAT COULD RESULT IN A CONSIDERABLE INCREASE IN PLANT SIZE (AND COST) FOR A GIVEN THRUPUT OF BIOMASS. RECOGNIZING THIS FACT, TWO ADDITIONAL METHODS FOR SOLIDS INJECTION WERE BUILT INTO THE PLANT:

- o A SYSTEM FOR FEEDING PRETREATED WOOD; AND
- o A SYSTEM FOR FEEDING DRY WOOD POWDER DIRECTLY TO THE REACTOR.

THE FIRST ALTERNATIVE SYSTEM FOR PRETREATING THE FEED INVOLVES A BATCHWISE COOKING OF THE WOOD CHIPS IN WATER IN AN ELECTRICALLY HEATED, AGITATED AUTOCLAVE AT A TEMPERATURE OF ABOUT 500 °F AND 700 PSIG (SLIDES 11 AND 12). AFTER COOLING THE RESULTING SLURRY IN AN EXTERNAL PUMP AROUND CIRCUIT THROUGH AN AIR COOLED HEAT EXCHANGER, THE COOKED WOOD IS SEPARATED FROM

THE AQUEOUS WASTE BY MEANS OF A SMALL CONTINUOUS VACUUM FILTER (SLIDE 13). THE WOOD SOLIDS ARE SOMEWHAT SIMILAR TO CHARCOAL IN APPEARANCE AND ARE MORE EASILY PROCESSED THAN THE DRIED CHIPS. THE SOLIDS ARE DRIED AND GROUND AND THEN PROCESSED AS PREVIOUSLY DISCUSSED. THE PRETREATED WOOD OFFERS THE ADVANTAGE OF MAKING A SLURRY WITH IMPROVED RHEOLOGICAL PROPERTIES SUCH THAT A 50% SLURRY CAN BE PUMPED AND, ADDITIONALLY, THERE MAY BE ENHANCEMENT OF THE REACTIONS.

IN THE SECOND ALTERNATIVE SYSTEM, SOLIDS GO DIRECTLY INTO THE REACTOR WITH THE REACTOR AT PRESSURE AND TEMPERATURE (SLIDE 13).

FOR THIS PART OF THE PILOT PLANT, A MECHANICAL FEED ARRANGEMENT INCORPORATING A ROTARY FEEDER WAS DESIGNED. IT BASICALLY CONSISTS OF TWO PRESSURE-BALANCED LOCK HOPPERS WHICH WILL BE USED ALTERNATELY. TO BE ABLE TO USE CONVENTIONAL ROTARY FEEDERS, THE LOCK HOPPERS WERE DESIGNED SO THAT THE FEEDERS ARE INSTALLED INSIDE AND, THEREFORE, ARE NOT EXPOSED TO HIGH DIFFERENTIAL PRESSURE. WHILE A ROTARY FEEDER CAPABLE OF WITHSTANDING A 4000 PSIG DIFFERENTIAL WOULD HAVE BEEN PREFERRED FOR BETTER ACCESS, IMPROVED MAINTENANCE, AND A SIMPLER LOCK-HOPPER DESIGN, SLIGHT VENDOR INTEREST FOR BUILDING SUCH A FEEDER WAS EVIDENCED AND SUCH A UNIT WAS NOT AVAILABLE.

THE LOCK-HOPPER SYSTEM FUNCTIONS IN THE FOLLOWING MANNER. A LOCK HOPPER IS FILLED WITH WOOD POWDER AT ATMOSPHERIC PRESSURE AND PRESSURIZED TO 4000 PSIG USING A CARBON MONOXIDE-HYDROGEN MIXTURE. THE SOLIDS ARE THEN FED TO THE REACTOR BY THE ROTARY FEEDER. WHEN THE LOCK-HOPPER IS EMPTY, THE PRESSURE IS

REDUCED, VENTING FIRST TO A SURGE TANK, AND THEN THE RESIDUAL GAS TO THE INCINERATOR. ONCE THE LOCK HOPPER IS VENTED TO ATMOSPHERIC PRESSURE, IT IS READY FOR THE NEXT CYCLE. THE PURPOSE OF THE SURGE TANK IS TO COLLECT MOST OF THE CARBON MONOXIDE MIXTURE FROM THE LOCK HOPPERS, SO THAT IT CAN BE RECOMPRESSED AND REUSED IN THE NEXT CYCLE.

HEAT IS SUPPLIED BY RECYCLE OF PART OF THE PRODUCT OIL THROUGH THE PREHEATER AS IN THE PREVIOUS OPERATIONAL MODE. WE WOULD EXPECT EVEN HIGHER SLURRY CONCENTRATION WITH THIS FEED METHOD.

PROBLEMS AND DIFFICULTIES

PRACTICALLY ALL THE REACTION PRODUCT THAT WAS PRODUCED DURING THE PREVIOUS CONTRACT PERIOD WAS VERY VISCOUS AT AMBIENT TEMPERATURES AND VIRTUALLY UNPUMPABLE EVEN AT ELEVATED TEMPERATURES.

RECENT OPERATIONS HAVE BEEN HAMPERED BY INADEQUATE HEATING OF ELECTRICALLY TRACED PIPING. AS A RESULT OF CONTINUING MECHANICAL DIFFICULTIES, THE HIGHEST MATERIAL CONCENTRATION ACHIEVED HAS BEEN ABOUT 35% PRODUCT OIL IN START-UP VEHICLE OIL. TO DATE, SEPARATION OF PRODUCT OIL FROM START-UP OIL, ANTHRACENE, HAS NOT BEEN MADE.

THE WOOD PROCESSING EQUIPMENT HAS GENERALLY FUNCTIONED WELL.

MOYNO PUMPS USED FOR OIL-WOOD SLURRY CIRCULATION WERE ORIGINALLY SUPPLIED WITH BUNA STATORS WHICH HAD POOR RESISTANCE TO THE ANTHRACENE OIL USED AS START-UP VEHICLE. REPLACEMENT WITH VITON HAS SHOWN IMPROVEMENT BUT FURTHER IMPROVEMENT IS DESIRE

MANY FAILURES OF POLYMERIC GASKETS, RINGS AND SEAL PARTS WERE

REPORTED AND REQUIRED CHANGE-OUT TO SUCH MATERIALS AS TEFLON, GRAPHITE, METALLIC PARTS, ETC.

HIGH PRESSURE SLURRY FEED PUMP CHECK VALVES HAD SHORT LIFE UNTIL STAINLESS STEEL PARTS WERE REPLACED WITH STELLITE. PACKING LIFE HAS BEEN SHORT BUT IS IMPROVING WITH CHANGES IN MATERIAL.

SERIOUS MECHANICAL DEFICIENCIES WITH THE SCRAPED SURFACE PREHEATER EXISTED. THE MECHANICAL SHAFT SEAL WAS MODIFIED EXTENSIVELY TO PROVIDE A DOUBLE SEAL WITH INTERMEDIATE PRESSURE LEVEL. THE SCRAPER BLADES ARE MECHANICALLY INADEQUATE AND HAVE REQUIRED FREQUENT REBUILDING.

AS SUPPLIED, THE REACTOR HEAD-TO-SHELL CLOSURE WAS NOT ADEQUATE FOR CYCLIC OPERATION AS IS COMMON IN A NEW PROCESS PILOT PLANT. REPLACEMENT WITH A GRAYLOC CLOSURE ELIMINATED THIS PROBLEM.

ONE MAJOR PROBLEM THAT STILL EXISTS CONCERNS THE REACTOR AGITATOR SHAFT SEAL. INSTEAD OF THE PACKLESS, MAGNETIC DRIVE SPECIFIED, A CONVENTIONAL DOUBLE SEAL WITH ELASTOMERIC PARTS WAS INSTALLED. THESE HAVE BEEN INADEQUATE. THE PREVIOUS CONTRACTOR REMOVED THE AGITATOR, AND WHEN THE REACTOR WAS USED, IT WAS WITHOUT AGITATION. EFFORTS ARE CURRENTLY UNDERWAY TO PROVIDE ADEQUATE EQUIPMENT TO RESTORE THE REACTOR TO THE PROCESS AS DESIGNED.

REACTOR PRODUCT PRESSURE LETDOWN VALVES HAVE HAD SHORT LIFE. THIS WAS NOT UNEXPECTED WHEN CONSIDERATION IS GIVEN TO THE EXTREMELY SEVERE ONE-STEP DROP FROM 4000 PSIG TO 5 PSIG. PARALLEL VALVES WERE INSTALLED TO PERMIT REPLACEMENT WITHOUT PROCESS INTERRUPTION. VARIOUS VALVE TRIM MATERIALS HAVE BEEN

USED. STELLITE HAS BEEN THE MOST SUCCESSFUL TO DATE. THE SMALL VALVE SIZE INHERENT WITH LOW CAPACITY AND HIGH PRESSURE DIFFERENTIAL COMPOUND THE PROBLEM.

SEVERAL FAILURES OF THE CARBON MONOXIDE COMPRESSOR DIAPHRAGMS OCCURRED. HEAD MODIFICATION BY THE MANUFACTURER ELIMINATED THIS PROBLEM.

NO SERIOUS ATTEMPT HAS BEEN MADE TO OPERATE USING THE PRETREATER MODE OF WOOD PREPARATION, TO DATE. THIS EQUIPMENT WILL BE USED LATER IN THE PROGRAM.

NO EFFORT HAS BEEN MADE TO OPERATE IN THE LOCK HOPPER FEED MODE. USE OF THIS EQUIPMENT IS SCHEDULED LATER IN THE PROGRAM.

AS PREVIOUSLY MENTIONED, PRODUCT VISCOSITY PROBLEMS TO DATE HAVE PRECLUDED USE OF THE CENTRIFUGE CLEANUP. HOWEVER, RECENT ENCOURAGING RESULTS INDICATE LOWER VISCOSITIES WHICH LEND THEMSELVES TO UTILIZATION OF THE EXISTING CENTRIFUGES FOR SEPARATION TESTING.

CORROSION PROBLEMS ASSOCIATED WITH
THE INCINERATION OF REFUSE

by

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INTRODUCTION

There has been increasing incentive in recent years for disposal of municipal refuse by incineration. The need to recover energy from waste material, coupled with the difficulty in obtaining adequate land-fill sites, has created a great deal of interest in disposal by incineration. In addition municipal refuse is being considered as a supplementary fuel for existing fossil-fuel power-generating stations and for industrial needs for process steam. However, the corrosion of heat recovery surfaces exposed to combustion products from the burning of industrial and municipal wastes has been a major problem in utilizing these materials as a source of heat energy. Research conducted by Battelle in recent years has demonstrated that chlorine in the refuse is the most important contributor to corrosion of boiler tubes.⁽¹⁻⁸⁾ The sulfur in the refuse definitely plays a part in promoting corrosion by chlorine, and other components which are not present in fossil fuels such as zinc and lead may contribute to the unusual amount of corrosion which can occur during incineration. Experiments have been conducted to investigate the inhibition of chloride corrosion by the introduction of relatively large amounts of sulfur into the fuel. One of the most convenient ways of achieving this result has been to utilize high-sulfur coal in cofiring with municipal refuse in a stoker-fired boiler. The system employed is different from others being investigated elsewhere, in that refuse which has undergone only shredding and magnetic separation is burned on a traveling grate in conjunction with high-sulfur coal.

CORROSION IN FIRING OF BULK REFUSE

Corrosion rates from burning of bulk municipal refuse were obtained by exposing specially designed probes to the combustion gas environment at the Miami County, Ohio incinerator. The design of the corrosion probe, which has been used with either 18 or 34 specimens, is shown in Figure 1. The specimens were machined from 1-inch (2.54 cm) schedule 40 pipe or equivalent tubing and were nested together with lap joints, as shown in detail A. The probe was inserted into the incinerator through a side wall and was mounted at a 90° angle to the flue gas stream. The section of the probe extending through the wall was water cooled. The specimens exposed within the incinerator were cooled by air flowing inside the tubular specimens. The specimen temperatures were controlled by regulating the amount of cooling air admitted to the probe.

Corrosion probe exposures up to 828 hours were carried out, and the corrosion rates of the various steels used as specimens were determined by the weight losses that resulted from the exposure. The data for the 828 hour exposure calculated to a basis of mils per month are presented in Figure 2. As seen from the figure, the weight losses increased with temperature and were especially high for the carbon steel and the low alloy steel. Over a metal temperature range of 250 to 1200° F (121 - 649° C) the high-chromium ferritic and austenitic stainless steel showed the best corrosion resistance. As a function of exposure time, the corrosion rate of carbon steel was found to be very high initially and then to drop rapidly, leveling off after about 800 hours, as shown in Figure 3. The effect of metal temperature is also shown by this data, which illustrate the increase in the corrosion rates as the temperature of the metal specimens was increased from 350 to 950° F (177 - 510° C).

DEPOSIT AND SCALE ANALYSIS

Both the bulk deposits and the corrosion product layers formed on the specimens were analyzed during this program to determine the reactions leading to metal wastage. The deposits were removed from all the probe

FIGURE 3. ISOTHERMAL CORROSION RATES FOR AL06 STEEL
VS EXPOSURE TIME IN BULK REFUSE INCINERATION

specimens in numbered sequence. Thus the variations in composition could be determined as a function of temperature when the deposits were analyzed. Analysis of the bulk deposits showed that chloride accumulated rapidly even at moderate HCl concentrations in the flue gases. Chloride concentrations ranging from 21 to 27 percent by weight were found on probes which were exposed for short periods of time ranging from 1.5 to 24 hours. Flue gases contained from 40 to 140 ppm HCl (corrected to 12 percent CO₂) during the time that these deposits were formed.

Eight analyses of typical refuse samples from the incinerator showed that the chloride content of the solid waste on a dry basis ranged from 0.32 to 0.79 weight percent, with an average of 0.49 percent. Based on an average 24 hour processing of 150 tons (136,080 kg) of waste at this incinerator, there would be about 1500 pounds (682 kg) of chlorine in the refuse. The sources of the chlorine are both inorganic, primarily as NaCl, and organic. Refuse sortings made at four different times at the incinerator gave values for plastic content of 3 to 6 percent. Of this about 1/5 was estimated to be polyvinyl chloride. Using the lowest value of 3 percent total plastic, the polyvinyl chloride would account for 900 pounds (409 kg) of the 1500 pounds (682 kg) of chloride in the refuse consumed daily. The remainder would be of inorganic origin. From these values it is obvious that large amounts of chlorine are available to cause corrosion.

The sulfur resembles chlorine in that its concentration built up rapidly in the deposits and leveled off after about 100 hours. On the higher temperature specimens the sulfur concentration was found to be somewhat lower, probably because of the volatility of some of its compounds. The inner layers of the deposit contained approximately twice as much sulfur as did the outer layers. Electron microprobe analysis of the corrosion scale layer showed that significant amounts of chlorine, sulfur, zinc, and lead were present at the interface of the tube metal and the scale (Figure 4).

Investigation by X-ray diffraction has demonstrated that a continuous layer of FeCl₂ exists at the interface with the metal. FeS occurs between the FeCl₂ and the overlaying Fe₂O₃ layer. Various other compounds, mostly sulfates, were identified in the deposits. About 20 different compounds have been identified as shown in Figure 5. On the higher

FIGURE 4. ELECTRON MICROPROBE PHOTOGRAPHS SHOWING DISTRIBUTION OF VARIOUS ELEMENTS IN THE CORROSION SCALE LAYER

FIGURE 5. SCHEMATIC DIAGRAM SHOWING LOCATION OF PHASES IDENTIFIED BY X-RAY DIFFRACTION

temperature specimens, it was found that the FeCl_2 layer melted and collected into small pools. The electron microprobe showed that a zinc compound was also present in this area near the metal.

CORROSION MECHANISMS

A number of chemical reactions are proposed to account for the formation of chlorides and sulfates in the deposits, as shown in Figure 6. Initial deposits are alkali metal oxides, which are then converted to chlorides by the actions of HCl . Some chlorides such as NaCl may be volatilized in the flame and deposited as such. It is believed that corrosion is initiated by reaction 1 in which chlorides are converted to sulfates by the action of SO_2 , oxygen, and moisture, thereby releasing HCl at the metal surface. The figure illustrates the reaction for potassium, and sodium acts the same way. The hydrogen chloride formed can then react with the iron surface to form ferrous chloride as shown in reaction 2, or it may be oxidized to elemental chlorine as shown in reaction 3. As indicated by the laboratory studies at Battelle and supported by the work of Brown, DeLong, and Auld⁽⁹⁾, the corrosive effects from HCl would not be expected to be severe below temperatures of about 600°F (316°C). Since FeCl_2 has been detected on corrosion probe samples exposed to temperatures well below 600°F (316°C), it is likely that corrosion by elemental chlorine has not been identified in incinerator and furnace gases, it is believed that it may play a role in the corrosion reaction. Metal chlorides on the tube surfaces can catalyze reaction 3 as is done in the Deacon process. The chlorine, which is formed only near the catalytic surface, would then combine directly with the iron as shown in reaction 4.

The molten salt phase which was found as an interface layer between the scale and deposit would act as a barrier to the motion of the gases in and out of the layer adjacent to the metal surfaces. Under oxidizing conditions, it would be expected that FeCl_2 would react with oxygen to form Fe_2O_3 as given by reaction 5. Once a scale formed on the metal tubes, such a cyclic reaction could occur. The mixed oxide in molten salt layers

- (1) $2\text{KCl} + \text{SO}_2 + 1/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2\text{HCl}$
- (2) $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$
- (3) $2\text{HCl} + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2$
- (4) $\text{Fe} + \text{Cl}_2 \rightarrow \text{FeCl}_2$
- (5) $4\text{FeCl}_2 + 3 \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{Cl}_2$
- (6) $\text{K}_2\text{O} + 2\text{HCl} \rightarrow 2\text{KCl} + \text{H}_2\text{O}$
- (7) $\text{Fe}_2\text{O}_3 + 3\text{K}_2\text{S}_2\text{O}_7 \rightarrow 2\text{K}_3\text{Fe}(\text{SO}_4)_3$
- (8) $2\text{KHSO}_4 + 3\text{Fe} \rightarrow \text{Fe}_2\text{O}_3 + \text{FeS} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$
- (9) $\text{K}_2\text{S}_2\text{O}_7 + 3\text{Fe} \rightarrow \text{Fe}_2\text{O}_3 + \text{FeS} + \text{K}_2\text{SO}_4$

FIGURE 6. CHEMICAL REACTIONS INVOLVED IN CORROSION

would limit the availability of oxygen, and retain the chlorine within the adherent scale. Similar corrosive conditions from deposited chloride were demonstrated by Cutler et al.⁽¹⁰⁾, particularly as they applied to burning fossil fuels containing chlorine. The possibility of oxidizing FeCl_2 to release elemental chlorine also was shown by Fassler et al.⁽¹¹⁾.

The formation of FeS in the corrosion product layer indicates that sulfur is also playing a part in the corrosion reactions. The alkali pyrosulfates and bisulfates are known to be very corrosive materials, and the potassium compounds in particular have low melting points. Hence corrosion by these materials as shown in equations 8 and 9 is a very likely possibility for the formation of FeS .

In order to make a more complete evaluation of chlorine and sulfur in the corrosion reactions, the concentration of these elements in the refuse was increased by the addition of either polyvinyl chloride (PVC) or elemental sulfur. As it was not feasible to conduct experiments with controlled additions with these materials over long periods of time, this program consisted of exposing corrosion probes for 10 hours. These short time experiments were intended to show differences in the corrosiveness of the combustion environment as the result of the increased concentration of chlorine or sulfur. With an increase of chlorine content of the refuse by PVC addition the corrosion rates leveled off at metal temperatures up to 900°F (482°C). However, at a metal temperature of 1100°F (593°C) the corrosion rate continued to increase linearly with the amount of PVC added.

When sulfur was added to the refuse, the chloride content of the deposits decreased significantly as shown in Table 1. The effect was particularly pronounced in the $700\text{--}750^\circ \text{F}$ ($371\text{--}399^\circ \text{C}$) temperature zone where chlorine reached a concentration of 7.5 weight percent in the deposits after 8 hours of operation with normal refuse. When .75 weight percent sulfur was added to the refuse the chloride concentration dropped to 1.9 percent, and when 1.5 weight percent sulfur was added the chloride concentration was further reduced to 0.1 weight percent. The effect was even more pronounced in the high temperature zone where the chloride concentration was reduced 25-fold by the addition of 0.75 weight percent sulfur, and below the detection limits for chloride when 1.5 weight percent sulfur was added. This decrease

TABLE 1. SULFUR AND CHLORINE CONTENT OF DEPOSITS WITH SULFUR ADDITIONS TO REFUSE

	Concentration (Wt %) With Indicated Sulfur Addition (Wt %)					
	None		0.75% S		1.5% S	
Metal Temperature, °F (°C)	745 (395)	1120 (695)	730 (390)	1125 (605)	740 (343)	1175 (635)
Sulfur	4.6	2.8	3.5	6.0	5.0	3.8
Chlorine	7.5	2.5	1.9	0.1	0.1	<0.1

in the chloride concentration in the deposits indicates that the added sulfur in the refuse forms sulfur oxides rapidly, which then react with the metal chlorides while still in the flue-gas stream. This rapid formation of sulfates left very little particulate chloride to collect in the deposit. The effect of the sulfur additions on the corrosion rate of Al06 steel is presented in Figure 7. At 300° F (149° C) metal temperature the corrosion rate decreased linearly with the amount of sulfur added. At higher temperatures the rapid decrease in corrosion rate began at the point of 0.75 weight percent sulfur addition. On the basis that the normal sulfur content of refuse is about 1.2 percent, these data indicate that when the total sulfur level in the refuse reaches 1 percent the corrosion rates can be expected to decrease.

REFUSE FIRING WITH HIGH SULFUR COAL

It was a logical step to proceed from the addition of sulfur to refuse to employing high sulfur coal as the source of the SO₂ needed to suppress chloride corrosion. Consequently additional work on the research program was directed to investigating the disposal of municipal refuse by co-firing with high-sulfur coal in a stoker-fired boiler, to demonstrate:

- (1) that corrosion of boiler tube materials in such a system would be minimal, and
- (2) that the sulfur oxide emissions from the coal would be reduced to acceptable levels by dilution of the coal with refuse and by the interaction of the alkaline components of the solid wastes with the sulfur

FIGURE 7. ISOTHERMAL CORROSION RATES OF A106 CARBON STEEL VS SULFUR ADDITIONS TO REFUSE

oxides. The coal-fired boiler at the Municipal Electric Plant, Columbus, Ohio, has been used for this program. This site was selected to represent boiler furnaces having grates on which final burnout of the refuse could occur. The boiler used has a spreader stoker and is rated at 150 thousand pounds of steam per hour, but it normally operates up to 125 thousand pounds per hour with a maximum electrical output of 12.5 MW.

Initial corrosion rates of A106 carbon steel as a function of the metal temperature during the combustion of various coals, coals plus refuse, and 100 percent refuse are shown in Figure 8. The results presented in the upper part of the figure for burning of bulk refuse were obtained at the Miami County incinerator, Troy, Ohio. The corrosion rates with refuse alone proved to be an order of magnitude greater than those found with coal or coal plus up to 42 percent refuse. In the lower portion of the figure the two data points at about 750° F (399° C) which showed the highest corrosion rates, represent the coal with 5 percent sulfur and are the result of sulfide corrosion. It should be emphasized that these data represent corrosion rates obtained in 8-hour probe exposure and are useful for comparing materials and refuse-coal mixes but should not be extrapolated to represent long-term corrosion rates. These rates drop off rapidly with time, as protective oxide layers are built up on the metal surfaces, and then level off at a much lower wastage rate. It is significant that when the sulfur content of coal reaches 5 percent the corrosion rate of carbon steel is controlled by the sulfur and not by the chlorine content of the refuse, at least up to the amounts of refuse used in these experiments.

CONCLUSIONS

The results of this experimental program have shown that the sulfur and chlorine contents of refuse have significant effects on the corrosion of metal surfaces exposed to hot combustion products. From the data collected it can be concluded that: (1) The conversion of chlorides to sulfates in the incinerator deposits by the action of SO₂ releases chlorine and HCl at the metal surface, thereby causing serious corrosion.

FIGURE 8. INITIAL CORROSION RATES OF A106 CARBON STEEL WITH VARIOUS FUELS

(2) Chloride corrosion can be made negligible by increasing the total available sulfur in fuel to equal 2 weight percent of the refuse.

(3) Co-firing of refuse with high sulfur coal up to a 60/40 mix on a Btu basis will not increase the initial corrosion rate beyond that of coal alone.

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MATERIALS OF CONSTRUCTION FOR GASIFICATION

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MATERIALS OF CONSTRUCTION FOR GASIFICATION

A J Mac Nab
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Gasification of solid hydrocarbons, by means of thermal-chemical reaction, to yield gaseous products of high calorific value can be accomplished in a variety of ways. Details of the process technology depend on both the feedstock to be processed and the end product desired. Basically, these are two categories of end product, low and high Btu gas. The feedstock variations are more numerous.

Each process variation includes a sequence of steps, some of which may be unique, most of which are common to all processes. Many of the units will not require anything unusual in the way of materials of construction. These process steps will have been used many times before, and the conditions to which materials are subjected are well within the capability of present technology.

The concerns with materials of construction for gasification have been twofold. One in dealing with unique and severe service conditions, demanding extraordinary properties, the other connected with the extraordinary size of certain individual equipment items projected for commercial units.

Most of the processes with which this writer is familiar were part of the DOE-GRI joint high Btu gasification program, and are at the large pilot plant stage of development. The problem areas discussed below, however, can apply equally well to other plants and even commercial gasification units.

The principal categories into which materials problems can be divided are

- 1 High-temperature corrosion
- 2 Erosion
- 3 Mechanical properties
- 4 Aqueous corrosion

We will consider each of these in turn with respect to causes and effects.

HIGH-TEMPERATURE CORROSION Most gasification reactions require temperatures of 1400-1800° F to proceed efficiently. At these temperatures the presence of corrosive gases and vapors can result in severe corrosion of both metal and ceramic structural components. Typical ingredients (Figure 1) in a gasifier atmosphere would be hydrogen, H₂S, CO, CO₂, NH₃, N₂, steam, and hydrocarbons. There may also be organic and inorganic acids, and inorganic salts.

Of the numerous reactions that are possible between solids and gases (Figure 2), and solids and liquids, sulfidation has frequently been identified as potentially the most severe. Very high rates of scaling are known to occur in reducing sulfide atmospheres at temperatures around 1000° F or less. The existence of condensed liquid films, such as fused salts or molten eutectic oxides and sulfides can aggravate the problem.

A major difficulty confronting designers is knowing the precise chemistry of the environment at each location within a gasifier reactor. Figure 3 illustrates how the gas composition varies from one level to another in one type of reactor only. There are numerous designs each with its own mode of operation, and operating conditions. The gas composition profile will change with each design and with each type of coal feedstock used. Furthermore, the gas compositions from spot analyses of an operating reactor are nonequilibrium mixtures until quenched.

For these reasons, laboratory research work accomplished to date must be viewed with caution. Working with a multicomponent environment of fixed predetermined composition and varying key components, one at a time, is a practical experimental approach, but clearly may fail to predict the worst cases, unless an uneconomically large program is undertaken.

In the complete absence of high-temperature corrosion data, it is necessary to conduct limited screening tests of various materials in artificial laboratory environments. But detection of the real problems comes from observation of fully integrated operating equipment, with commercial plant data being best of all.

HIGH-TEMPERATURE CORROSION . Continued

In the Metals Properties Council program on gasification, there have been many useful observations from laboratory screening studies. Rank ordering of alloys for corrosion resistance has essentially followed expected lines, but with some unexpected results. In general, resistant alloys require greater than 25 percent chromium. High nickel alloys with insufficient chromium rapidly deteriorate by sulfidation. Sulfidation in a low oxidizing potential environment appears to be the key mechanism. Some typical data are shown in Figure 4. But it has also been demonstrated that breakdown of protection occurs where low melting eutectic sulfides are formed. Such a eutectic appears between 1800 and 1850° F for many alloys. Excursions to 1850° F operating temperatures can be disastrous for these materials.

EROSION Because it is necessary to move solid particulate material continuously through the process equipment, erosion is an inherent problem. Figure 5 illustrates some of the areas of concern in a typical gasification process. Note the variety of solid materials ranging from raw coal and coal char, to ash. These solids may be transported by liquid carrier as a slurry or pneumatically conveyed by gas or vapor.

Figure 6 summarizes some of the conditions which might be expected. The conditions are categorized for the types of equipment involved.

The types of erosion experienced range from sliding wear as a result of moving bulk solids to impingement attack by high velocity fines on turbine blades. One of the modes of erosion that has attracted a great deal of research is the combined effect of corrosion and erosion. This is of especial concern where high-temperature scales may be necessary for alloy protection, but are endangered by the presence of abrasive solids. Another area is the performance of refractories and ceramics at high temperatures under particle bombardment.

For many of the applications in a coal gasification plant, there is satisfactory prior experience to fall back on. For example, conventional equipment exists for the handling and sizing of dry coal. Wear resistant materials, such as the manganese steels and chrome-nickel white irons are suitable for severe abrasive applications. Where corrosion is involved, stainless steels or rubber linings may be needed. These find wide application in pumps.

EROSION Continued

Research has been in progress on the more difficult applications involving high pressure drops with solids laden corrosive gases at high temperature. Materials, such as titanium diboride, hot pressed boron carbide and chemically vapor deposited silicon carbide appears to have excellent prospects for such applications, and work is in progress on the design aspects of their use.

MECHANICAL PROPERTIES Having selected a material for adequate corrosion and erosion resistance, it is then necessary to consider its mechanical properties. For very high temperature applications, this can have equal importance with corrosion, one or the other being the life determining factor. There are two areas where the effect of temperature may be of concern, 1) in pressure vessel design where design temperatures encroach on the creep range of the material, and 2) where internal vessel components may be exposed to the highest process temperatures.

In the first case, it is often possible to reduce the design temperature by insulating the vessel wall, or by using external water jackets. Where this is not possible, then design must be in accordance with rules developed by the ASME and requires more stringent calculations. A complication arises when the effect of the environment on the on the long term properties is questioned. While these effects are not well quantified, there is consolation in the fact that the safety factors employed in existing process vessels for similar service have apparently been adequate, based on performance. This is not to say a better understanding is not needed.

Current research in these areas is concerned with developing creep, stress to rupture and fatigue data at very high temperatures, say up to 2000° F, for a variety of suitable alloys. In addition, the effect of the coal gas environments on these properties, as compared with data in air, is being obtained. Another approach is the development of alloys with superior properties to presently available commercial alloys for use in pressure vessel construction.

Both approaches will hopefully result in more options for the designer in selecting materials, and at the same time confirm or improve reliability.

AQUEOUS CORROSION There are several locations in a gasification plant where aqueous phases can cause significant corrosion. The most obvious and possibly most important is in the raw gas quench systems, where water saturated with acid gases, ammonia, and tar acids must be handled in large vessels and piping at temperatures up to 460° F and pressures to 1000 psig.

Depending on pH general corrosion attack of carbon and low alloy steels could be serious. Further, the high temperature and pressure accentuates the seriousness of a stress corrosion cracking failure.

Again, preliminary studies have been undertaken by the Metals Properties Council to assess the severity of attack in laboratory environments designed to duplicate expected commercial plant quench waters. To overcome the problem of running large numbers of tests and to facilitate observation of the effects of individual parameters, a statistically designed experiment was conducted. Again, caution is needed in using the data, but they have served to indicate factors affecting the corrosion of carbon steel and provide a preliminary basis for comparing systems.

In general, it has been found that carbon steel is susceptible to severe general attack under certain combinations of corrodents. Under the same conditions, Type 304 stainless is resistant to general corrosion, but shows a tendency to pit. Type 316 stainless steel has shown no attack. Neither grade of stainless has cracked. Minor components, such as chloride, phenol and cyanide appear to exert as much influence on corrosion of steel as H_2S , CO_2 , and NH_3 . Combinations of these components can either accelerate or decelerate attack.

CONCLUSIONS Biomass feedstocks for the types of process we have discussed will introduce new considerations. Depending on the chemistry of the biomass, corrosion problems may be more or less severe. Changes may occur in the location of severest attack. Erosion problems may greatly diminish because of the softer material being handled. These topics should form the basis of discussion for the remainder of this workshop.

MATERIALS OF CONSTRUCTION FOR GASIFICATION

Viewgraphs Presented

by

A. J. MacNab

C. F. Braun & Company

Alhambra, California

FIGURE 2
HYGAS PROCESS SCHEME

TYPICAL RAW GAS COMPOSITIONS - WESTERN COAL

H₂O	20-35%	CH₄	10-13%
H₂	16-22%	NH₃	0.4%
CO	9-19%	H₂S	0.03-0.2%
CO₂	4-19%		

TEMPERATURES 1350-1700°F

PRESSURES 150-1200 psig

TRACES OF ORGANICS, HCN, COS AND N₂

BAT12.2

IGT HYGAS PROCESS

DAY 1/24

1800°F - 1% H₂S - 1000 HRS.

POTENTIAL AREAS FOR EROSION

BA112.3

<u>EQUIPMENT</u>		<u>SOLIDS HANDLING</u>	<u>REACTOR FEED</u>	<u>PRODUCT GASES</u>	<u>EFFLUENT DISPOSAL</u>
COILS, HXs, CHANGERS, COLUMNS, FEEDERS, VALVES		COAL, CHAIR, ASH, OTHER	COAL, CHAIR, OTHER, SLURRIES OR PNEUMATIC	CHAIR, ASH, PNEUMATIC	CHGR, ASH, SLAG, OTHER, SOLIDS OR LIQUIDS
PIPING, PUMPS, VALVES, REACTORS					
PIPING, CYCLONES, DUCTORS					
TANKS, VALVES, PIPING, MACHINERY					

TYPICAL EROSION CONDITIONS IN COAL GASIFICATION

PROCESS AREA	EQUIPMENT	CONDITIONS
COAL PRESSURIZING	PUMPS	20-50 wt% COAL SLURRY -10 TO +80 MESH; 150°F.; 1000 psig 25-30 ft/sec
	PIPING	3-10 ft/sec
GASIFICATION	PNEUMATIC TRANSFER PIPING	a) 20-30 fps 0.3 - 0.5 lbs/acf b) 50-75 fps 0.05 lbs/acf 0.12 lbs/acf
	CYCLONES	
	CHAR SLURRY VALVE	25% SOLIDS SLURRY 1000 psi → 15 psi
POWER RECOVERY	TURBINE BLADES	CHAR, ASH, DOLOMITE 0.04 - 0.16 grams/acf <20 μ 100-1600 fps BLADE SPEED

TABLE 2
PHYSICAL AND MECHANICAL PROPERTIES OF
ALLOYS REQUIRED FOR USE AS CASIFIER
INTERNAL COMPONENTS

PHYSICAL PROPERTIES

DENSITY
SPECIFIC HEAT
THERMAL EXPANSION
THERMAL CONDUCTIVITY
POISSONS RATIO
MODULUS OF ELASTICITY
EMISSIVITY
MELTING POINT

MECHANICAL PROPERTIES

SHORT TIME TENSILE PROPERTIES
HARDNESS
TOUGHNESS
CREEP STRENGTH
FATIGUE CHARACTERISTICS
CREEP RUPTURE STRENGTH

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POTENTIAL CORROSION PROBLEMS IN ACID HYDROLYSIS PROCESS

Viewgraphs Presented
by

Robert B. Puyear
Monsanto Company
St. Louis, Missouri

Potential Corrosion Problems in Acid Hydrolysis Process

1. Process Assumptions:

Sulfuric acid will be added to cellulose-water slurry either hot (200°C) or cold (room temperature).

Other acids, for example HCl, may be used.

Heat may be added through steam injection or through heat exchanger.

Equipment is within the normal size range for CPI process equipment.

2. Potential Corrosion Problem Areas

Low temperature portion of process should present no unusual corrosion problems. Conventional, and relatively inexpensive materials should be satisfactory. Precise materials selection would depend on specific process conditions and equipment size.

High temperature process conditions are outside the normal range for published corrosion behavior for most materials.

Corrosion problems are potentially serious and may be affected by subtle process variations.

The following discussion explores some of the obvious - and perhaps not so obvious effects:

1. Temperature

Chart - Cast alloys in 70% H_2SO_4

Chart - Carpenter 20Cb and 20Cb3

Chart - Hastelloy C-276 (Isocorrosion)

Chart - 5% H_2SO_4 - 150-300°F - Hastelloys B and C-276

2. Temperature and oxygen content

Chart HCl (10 and 25%) N_2 and air - 2000 psi

3. Chloride content, acid anion

Chart

4. Deposits

Crevice corrosion (note previous chart)

5. Velocity

6. Metal ion content - reduce or accelerate corrosion

7. Organic molecule. Possible inhibitor effect

8. Heat transfer surfaces

Materials for high temperature service

Metals -

- Fe-Ni-Cr-(Mo,Cu) alloys

Ceramics -

- Glass - Chart - Glassteel in sulfuric acid

- Other - Concern over mechanical integrity in larger sizes.

Plastics -

Fluoropolymer - PTFE up to 500°F (260°C)

Lined steel pipe and fittings up to 8" pipe size

CORROSION OF CAST ALLOYS IN 70% H_2SO_4
(<0.1 ft/sec)

CHEMICAL COMPOSITION OF CAST ALLOYS

Alloy	Percent										
	<u>C</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Si</u>	<u>Cu</u>	<u>Cb</u>	<u>Ti</u>	<u>Fe</u>	<u>Mn</u>	<u>Other</u>
1. Results of Specific Chemical Analyses											
304SS Cast	0.060	17.74	8.63	0.30	0.82	0.10	-	-	Bal	-	-
316SS Cast	0.041	19.58	9.69	2.16	1.50	0.07	0.10	0.08	Bal	-	-
Durimet 20 Cast	0.061	19.26	31.53	2.28	1.05	1.06	0.10	0.10	Bal	-	-
Hastelloy B Cast	0.046	0.44	62.11	26.63	0.76	0.10	-	-	-	-	-
Hastelloy C Cast	0.078	15.27	56.45	17.51	0.79	0.09	-	-	-	-	-
Worthite	0.12	17.21	25.66	2.79	3.02	0.58	-	-	Bal	-	-
LaBour R-55	0.036	24.74	52.01	7.77	4.05	0.91	-	-	Bal	-	-
Elcomet K	0.078	16.63	27.16	2.89	1.91	2.56	-	-	Bal	-	-
Illium B	0.031	27.99	52.75	8.76	3.25	6.05	-	-	-	-	-
Illium P	0.22	25.80	8.17	2.11	0.80	2.73	-	-	-	-	-
Illium 98	0.29	29.87	54.76	9.00	0.76	5.40	-	-	-	-	-
3. Nominal Compositions											
Durco D-10	-	23.00	57.00	4.00	-	8.00	-	-	-	1.00	W 2.00
Durichlor	0.85	-	-	3.00	14.5	-	-	-	Bal	0.65	-
Duriron	0.85	-	-	-	14.5	-	-	-	Bal	0.65	-
Hastelloy D	0.12	1.00	85.	-	8.50- 10.00	2.00- 4.00	-	-	2.00	0.50- 1.25	Co 1.50

Resistance of Hastelloy C-276 to Sulfuric Acid

Corrosion by Five Weight Percent Sulfuric Acid

Temp. °F (°C)	Hastelloy C-276		Hastelloy B	
	a	b	a	b
150 (66)	<1	<1	5	6
175 (80)	1.2	1.3	7	7
214 (Boil) (101)	18	22	2	2
250 (121)	61	67	30	32
300 (149)	100	104	38	43

A. Asphahani
Stellite Division
Cabot Corp.

Results of Corrosion Tests in 10% Sulfuric Acid

Corrosion Rate (Mil Per Year)

<u>Material</u>	<u>Boiling Point 104°C(220°F)</u>	<u>220°C(390°F)</u>
Hastelloy B	2	120
Hastelloy C	50	1140
317 stainless steel	--	2000
Carpenter No. 20	24	2600
Molybdenum	nil	nil
Tantalum	nil	0.2
Silver	0.4	168

Effect of Temperature and
Oxygen Concentration on Corrosion
by Hydrochloric Acid

(Tests made in sealed glass tubes under 2000 psi pressure)

C		Corrosion Rate - Mils Per Year			
Temperature		Hastelloy B		Hastelloy C	
OF	OC	100% N ₂ Atmosphere	80% N ₂ -20% O ₂ Atmosphere	100% N ₂ Atmosphere	80% N ₂ -20% O ₂ Atmosphere
10 Wt Percent HCl					
156	69	-	85	-	114
212	100	9	262	228	293
275	135	20	402	-	>1000
25 Wt Percent HCl					
156	69	2	58	40	91
212	100	8	155	612	449
275	135	49	336	-	>1000

Ref: Corrosion Resistance of Union
Carbide Alloys, December, 1966

Behavior of Stressed Coupons in
Chloride Solutions at 141°C (285°F)

(One Month Exposures)

Alloy	2 Wt% NaCl	<u>Corrosion Rate, Mils Per Year</u>		
		0.8%NaCl +0.2%H ₃ PO ₄	4%NaCl +1.7%H ₃ PO ₄	0.8%NaCl +0.5%CH ₃ COOH
304	0.8 ³	5.6* ^{1,2}	6.1 ^{1,2}	1.2 ^{1,3}
304L	3.3 ³	3.9* ^{1,2}	5.4 ^{1,2}	0.8 ^{1,3}
316		0.7* ^{1,2}	4.4 ^{1,2}	0.3 ^{1,3}
316L		0.3* ¹	1.8 ¹	<0.1*** ^{1,3}
Carpenter 20cb3		2.9** ^{2,3}	3.0 ^{2,3}	<0.1
Incoloy 825		1.1** ^{2,3}	<0.1	<0.1
Haynes 20MOD	<0.1	<0.1**	<0.1	<0.1
Hastelloy G	<0.1	<0.1**	<0.1	<0.1
Hastelloy C-276	<0.1	<0.1**	0.3	<0.1

Notes:

1. Stress corrosion cracking

2. Crevice corrosion

3. Pitting

* 10 days only

** Autoclave leaked last 20 days, exact environment not known

*** One specimen out of two cracked

Reference: "Effect of Acids on the Stress Corrosion Cracking of
Stainless Materials in Dilute Chloride Solutions,
A. I. Asphahan, Stellite Div., Cabot Corp.

NOMINAL CHEMICAL COMPOSITION (Weight Percent)

<u>ALLOYS</u>	<u>Fe</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Mn</u>	<u>Si</u>	<u>Cu</u>	<u>C</u>
304	Bal	9	19	-	2*	1*	-	0.05
304L	Bal	9	19	-	2*	1*	-	0.03*
316	Bal	12	17	2.5	2*	1*	-	0.05
316L	Bal	12	17	2.5	2*	1*	-	0.03*
(1) Carpenter 20 Cb3	Bal	33	20	2.5	2*	1*	3	0.04
(2) Incoloy 825	30	Bal	21	3	1*	0.5*	2	0.04
(3) HAYNES alloy No. 20 Mod.	Bal	26	22	5	2.5*	1*	-	0.05*
(3) HASTELLOY alloy G	20	Bal	22	7	1.5	1*	2	0.05*
(3) HASTELLOY alloy C-276	5	Bal	16	16	1*	0.8*	-	0.02*

* Maximum

(1) Registered Trademark of Carpenter Technology Corporation

(2) Registered Trademark of International Nickel Company, Inc.

(3) Registered Trademark of Ccbot Corporation

CORROSION RESISTANCE OF GLASTEEL 3300

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LIQUIFACTION OF BIOMASS

by

J. Wilson

Shell Development Company

Houston, Texas

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Wind Energy

WIND ENERGY DESIGN

by

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At present Sandia Laboratories has three vertical axis wind turbines (VAWTs) in operation near Albuquerque, NM. Blades on these VAWTs are 17-m, 5-m, and 2-m in diameter. The 17-m VAWT has been tested for 2 years in both two- and three-bladed configurations. The 5-m VAWT has been tested for 5 years, again in both two- and three-bladed configurations. The 2-m VAWT is a wind tunnel model that has been tested for only 1 year in both two- and three-bladed configurations. All three turbines have blade diameters at blade centerlines that are the same as the blade height, for a height-to-diameter (H/D) ratio of 1:1.

The 17-m VAWT, which is rated at 60 kW output, has four guy cables and a rotating, tubular, heavy-walled steel blade tower. The 5-m VAWT, rated at 4 kW output, has four guy cables, a rotating, tubular steel blade tower, and an internal stationary tubular steel tower to carry the guy cable and top bearing loads. The 2-m VAWT, rated at less than 1 kW output, has four guy cables and a rotating, truss-type blade tower.

From hundreds of hours of testing and several cost studies of specific VAWT designs, Sandia Laboratories has established some design parameters that appear to produce the cheapest electrical energy and are still practical to design and build. These designs are based on present technology of aerodynamics and materials.

VAWT Design Parameters

- Brakes must be able to stop the VAWT at conditions of a 25% over-speed from rated speed in a 90 mph wind.
- Must operate in a 60 mph wind.
- Must withstand a 150 mph wind in nonoperating condition.

- Must operate in a temperature range of 120°F to -40°F.
- Must operate for 30 years, or 10^8 cycles.

VAWT Materials (refer to Fig. 1)

<u>Number</u>	<u>Item</u>
1	ASTM-A36-steel - air terminal
2, 17	QQ-B-613-brass - slip ring
3, 15	carbon - brush
4, 14, 26	copper - cable
5	ASTM-A36-steel - cable, bearing attachment
6	steel - Rotek bearing
7, 16	ASTM-A36-steel - blade, bearing attachment
8	ASTM-A36-steel - blade tower
9	steel - bridge strand, Class B zinc coated, guy cable
10, 13	6061-T6-aluminum - blade clamp
11	6063-T5-aluminum extrusion - blade
12	6063-T5-aluminum extrusion - blade joint
18	ASTM-A36-steel - u-joint
19	bronze - bearing
20	steel - transmission
21, 29	asbestos - brake, clutch lining
22	steel - brake caliper
23, 24	ASTM-A36-steel - brake, clutch discs
25	electrical generator
27	ASTM-A36-steel - guy anchor
28	steel reinforced concrete
30	steel - hydraulic clutch

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Blades are among the most expensive parts of the VAWT. At present the cheapest blade is thought to be made of 6063 aluminum in the T5 condition. This aluminum is extruded straight and then formed to the required shape. It has a tensile ultimate strength of $32,000 \text{ lb/in}^2$, a tensile yield strength of $28,000 \text{ lb/in}^2$, a fatigue limit of $10,000 \text{ lb/in}^2$, and an elongation of 16%. Design experience and past testing show that the blade stress can be limited to $6,000 \text{ lb/in}^2$ to achieve a stress level well under the fatigue limit.

The blade will be treated with a chemical film.

A VAWT can be so large that the blade is too long for convenient shipping. In that case the blade may be made in more than one piece and then joined at assembly by inserting aluminum doubler extrusions into the blade cavities and riveting the blade extrusions to the doubler extrusions. This design achieves a smooth aerodynamic surface at the blade joints.

Blade clamps join the blade at the ends and fasten the blade to the blade tower. These clamps are placed on the outside of the blade to achieve a large section modulus to withstand the blade root loads. At the blade root, the aerodynamic performance of the blade is not important because of the low speed of the blade and the low blade moment. The blade clamps are formed 6061-T6 aluminum sheet treated with a chemical film and painted with epoxy paint.

Because of aerodynamic requirements, the blades are among the most difficult VAWT parts to design and manufacture. Blade structural integrity must be maintained within the required aerodynamic shape. Other

VAWT parts have a wider choice of materials. In general, part size can be increased to a point where lower strength and cheaper materials can be used. More space is available without severe aerodynamic restrictions.

The blade tower, of welded ASTM-A36 structural steel, is rolled and welded into appropriate shipping lengths of less than 50 ft. It is designed generally for a maximum bending section modulus and to resist buckling. A minimum tower weight is thus achieved that saves material and reduces bearing loads to a minimum. The tower has a surface finish of primer and epoxy paint.

The top bearing is a Rotek bearing that can simultaneously withstand thrust, radial, and moment loads. One side of this bearing is bolted to the top of the blade tower, and the other to the guy cable attachment.

The top guy cable attachment to the VAWT is of welded ASTM-A36 steel with a primer and epoxy paint surface. This part has three functions; to attach the guy cables, to attach the bearing, and to support the air terminal and brushes for lightning protection.

The guy cable material is a Class B, zinc coated, steel bridge strand, which is used to achieve rigidity. The cable itself is approximately 10 times as strong as required by the maximum predicted cable load, but the bridge strand is selected to achieve the rigidity necessary to prevent resonant frequencies within the operating range. Bridge strand can achieve a modulus of elasticity in excess of 22,000,000 lb/in². For a more severe environment, a Class C zinc coating can be used on the cable. Cable end fittings are zinc coated steel.

The bottom of the blade tower is attached to a universal joint that permits relative motion without bending of the blade tower and the transmission shaft. The universal joint material is steel with bronze bushings at the four bearing points.

The transmission, which is a steel-cased gear box of the appropriate size to transmit power from the VAWT to the generator, has a gear ratio that provides an 1800 rpm output shaft speed to the generator. The VAWT is built directly upon the transmission shaft so that the transmission thrust bearing also supports the VAWT. This saves the costs of a thrust bearing and a platform to hold the thrust bearing.

The brake is located on the high speed shaft of the transmission, a location that permits the use of a lower torque braking system than does a brake situated on the low speed shaft. The size of the brake disc is determined by the amount of energy to be absorbed and by the thermal stress level permitted within the steel selected. The thermal stress is determined by the VAWT stopping time and the amount of differential temperature permitted. The brake caliper is a commercial product for all turbines except large ones. For large VAWTs the caliper may need to be of a specially designed size to cover more disc area and to provide more hydraulic force for higher torque.

VAWTs are not self-starting by the wind force; they must be started by some outside force. The generator can be used as a motor for this purpose. A clutch located between the motor and the transmission provides a controlled starting torque to the VAWT. The clutch discs are steel and the starting time and thermal stress determine the disc material and size.

Foundation and guy cable anchors are of steel-reinforced concrete. VAWT forces and the site geology determine the size and shape of these items.

The VAWT lightning protection system is designed primarily to protect the bearings at the guy cable attachment and in the transmission, although the generator is grounded to the same grounding system. This system consists of a steel air terminal at the top of the turbine that is long enough to provide a 120 degree cone of protection. The air terminal is connected to the guy cables through the VAWT structure. The top of the rotating blade tower is connected to the guy cables above the bearing by a brass slip ring, carbon brushes, and copper cables. The guy cables are also connected to ground by copper cables. The bottom of the blade tower is connected to ground by a brass slip ring, carbon brushes, and copper cables above the transmission. Since the inductance of the blade tower is much lower than that of the guy cables, and since lightning presumably does not go around corners, the main path from the air terminal to ground would probably be through the blade tower.

DESIGN PARAMETERS FOR SMALL WIND SYSTEMS

by

J. F. Boland

Presented by

Roger Moment

Rockwell International

Golden, Colorado

Introduction

The Rocky Flats Wind Systems Program, operated for the Department of Energy by Rockwell International, was organized in 1976 to support DOE (then ERDA) in establishing small wind energy conversion systems as a viable, cost-effective alternate energy source. These small systems would have outputs less than 100kW and typical rotor diameters less than 30 m (100 ft). To provide data helpful in this development work, a test center for small wind systems has been established at the DOE Rocky Flats Plant about 30 miles northwest of Denver. When fully operational, this center will be capable of simultaneously field testing up to 50 small wind systems. Commercially available systems are now being tested at this facility. In the future, testing will be conducted on prototype systems being developed by private industry either independently or with financial support from DOE. Data obtained during the performance and reliability testing at Rocky Flats will be available, through reports, to the manufacturers and the general public.

Objective

An objective of the DOE wind energy program is to stimulate the early commercialization and widespread use of small wind systems. To this end, Rocky Flats is funding competition in the design and fabrication of wind systems in a range of sizes which will satisfy a variety of applications. Common to all of these system development projects is the goal of achieving an energy cost which is competitive with the cost of conventionally derived energy (4 to 12c/kWh).

Problem

Two factors which strongly affect overall energy cost are the initial capital cost of the system and the maintenance cost over its lifetime.

If the system is underdesigned, a low capital cost might be achieved, but at the expense of reliability. On the other hand, overdesign can result in such a high capital cost that the system is priced out of any substantial market. A solution to this dilemma is for the designer to be knowledgeable in his selection of materials and components, selecting and sizing them to meet the wind machine's needs. In many instances, cost savings can be achieved by choosing standard off-the-shelf parts wherever they are appropriate and using specially built parts only when necessary. A knowledge of the intended applications and the range of environmental conditions into which the system will be placed is necessary in arriving at the choice of materials to be used. Cost versus performance trade-offs need to be performed on all components during the design stage in order to arrive at the most cost effective solution. This is not a simple task. In operation, all the wind systems components are interrelated. Varying the design of any one can have a cascading effect throughout the machine, not only on its durability, but on its cost as well.

The subject of this workshop, materials reliability, along with design deficiency, have been at the heart of many failures which have long plagued wind systems, both large and small. The numerous failures experienced with commercially available wind systems at Rocky Flats during the past two years have been disheartening. Most of the dozen or so systems examined thus far have experienced serious failures of some sort.

One such failure, which ended in the near total destruction of a wind system, apparently began as a small corrosion-induced crack on the leading edge of the aluminum alloy blade, where it attached to the rotor. This crack propagated unnoticed during two years of operation, until it was about two-thirds of the way through the blade chord. Finally, the blade broke during a sustained windstorm. If this damage had been confined to the blade, the cost of repair would have been minimal. However, design of this machine incorporated guy cables to support the blades, and when the blade failed, it remained attached to the rotor hub by its cable, though free to move about. As it apparently happened, the broken blade became tangled with the intact blade and the severe forces resulting from the out-of-balance rotor caused the subsequent failure of a large, aluminum

alloy casting which attached the wind turbine to the support tower. As a result, the entire wind system fell from the tower, sustaining additional, severe damage upon impacting the ground. The system, which would now cost over \$30,000 to replace, was a total loss.

Not only can a simple material fault such as this result in a large financial loss, but it could also result in damage to nearby structures or even in severe personal injury. Such failures of rotating equipment, weighing over 1000 kg, located on 12 to 30 m (36 to 90 ft) towers will not go unnoticed by insurance companies. The refusal of such companies to underwrite small wind systems could severely inhibit their commercialization and prevent the small wind system industry from reaching maturity.

Clearly, the subject of material selection and reliability is of utmost importance to the designers and manufacturers of small wind systems. This has become painfully evident to several companies, some of whom have been in the field for years. One worry is that many of the numerous new firms entering this field each year will repeat the mistakes of their predecessors in their haste to get hardware into the marketplace.

Design Concepts

The variety in the design of wind machines which have been conceived over the years is great indeed. The more proven concepts have recently re-emerged and are being modified and brought up to date by incorporating modern technology in the designs. Most of the currently available systems consist of two or three blades rotating about a horizontal drive shaft, in either the upwind or downwind position with respect to the tower. A sketch of a typical system of this type, showing the relationship of the major components, is shown in Figure 1. Several systems are being developed which have the blades rotating about a vertical axis. The work on one such rotor type, the Darrieus concept, is being described in another report at this workshop. The "Cycloturbine" and "Giromill" are other vertical axis systems which use straight articulated blades rather than the fixed, hooplike blades of the Darrieus.

Generally, on horizontal axis systems, a control mechanism is provided by which the blades can be varied in pitch. Such controls are used to provide self-starting capability and also to produce a relatively constant rotation once the rotor reaches its rated speed. These controls may also be used to orient the blades in either a full feather or fully stalled position (depending on the system design), in order to protect the rotor from overspeed in high winds. This control mechanism may be activated by an active device located in the nacelle or rotor hub, or it can be achieved by passive means, such as pendulum flyweights attached to the root of each blade. Centrifugal force tends to re-orient these flyweights and this motion is transmitted to the blades by a twisting or pitching moment which positions them for feather or stall. Internal mechanisms consisting of hydraulic or electro-mechanical devices, which sense the rotational speed of the main drive shaft, are often used to control the rotor speed of larger wind systems.

The rotor is the component which receives most of nature's abuse, passing it along to the remainder of the system in the form of vibratory loads, centrifugal and thrust forces, gyroscopic forces and the like. Interestingly, an author once noted that the modern wind rotor was actually a fatigue machine, which only incidentally generated electricity. In our more sarcastic moments, while we traverse the Rocky Flats landscape trying to collect pieces of blades in order to complete a failure report, we are inclined to consider such viewpoints as too prophetically true.

Material and Component Selection

Considering the growth in electrical consumption by the average farm or rural residence compared to that of 30 or 40 years ago (when small wind systems were last in vogue), it is apparent that the present generation of wind systems must be built much larger to satisfy the user's need. A wind machine having a 10 m (33 ft) diameter rotor will produce enough energy to meet most residential needs, if the wind system is located in a fairly windy region. This is more than twice the diameter of most

commercially available wind systems and it forces the designer to consider blade materials other than wood, which was successfully used on the older, smaller systems.

Aluminum and fiberglass reinforced plastics (GRP) have become leading choices of material for today's blades. Aluminum alloy blades are being made by direct extrusion or by fabrication from sheet stock. Newly developed fiberglass construction techniques, such as filament winding and pultrusion, have placed GRP blades into competition, both structurally and economically, with metal. Chemical foams, expanded into a closed die which may contain metal or other reinforcing materials, are also being evaluated as a means of making a strong yet lightweight blade.

The relatively slow rotational speed of most wind rotors (50-200 rpm) compared to the high shaft speed (900 to 1800 rpm) needed by most alternators or generators, requires the use of a speedup device. This speed increaser usually consists of a gearbox, but chains and sprockets or belts and pulleys have also been used. The operating lifetimes and efficiencies of these devices are generally known, but they do require periodic maintenance such as component servicing and replacement as well as lubrication. When wind systems are installed in cold environments, problems can occur with drive belt flexibility and lubricant viscosity.

Likewise, the electric generator is a component about which much is already known. Depending upon the buyer's need for ac or dc power, a variety of generators and alternators are available. Some require special equipment for interconnection with a utility power network. The low operating temperature which can be encountered by wind systems places emphasis on the materials used in the generating equipment. To qualify for trouble-free operation below about -30°C , special materials and bearings may add 30 to 40% to the cost of this component.

Some interest exists in the use of a direct-driven, low speed alternator, using strong permanent magnets. Such a device would eliminate the need for the speed increaser and hopefully provide for a more efficient,

reliable and maintenance-free system. Considerable development may be needed in order to bring costs down. One problem is maintaining a relatively small air gap in a large diameter generator. Development will probably be concentrated in the design of the magnets and poles so that high output voltage and low internal flux leakage can be obtained, while concurrently reducing noise and vibration caused by magnetic effects.

Operating Parameters

The wide range of environmental conditions in which small wind systems must operate is certainly a driving factor affecting the system cost. To be cost-effective and marketable, a wind system must have a long useful life (for example, 25 years) and be able to operate in a variety of climates and wind regimes throughout the United States and in other parts of the world. They must be designed with these conditions in mind. Some of the more extreme conditions that might be encountered in certain areas of the world are listed in Table I; however, all of these climatic and environmental conditions will probably never be present at any one location. Actually most wind machines will be installed in much more benign environments. It will, therefore, behoove manufacturers to offer options in those components where additional strength, corrosion resistance, etc., are needed to increase the chance that a system will survive in severe situations. In this way, the basic system cost will remain acceptable to potential buyers in areas where many of these extremes do not commonly occur.

Maintenance

Because of the difficulty, expense and hazards involved in performing repairs and maintenance on a wind system located on a tall tower, designers are encouraged to select critical components and parts that will have a long mean time between failures. Materials of construction should be chosen carefully so that atmospheric, galvanic or stress corrosion do not compromise the life or performance of the system. The need for regular downtime for maintenance such as greasing, changing oil,

painting, etc., should be minimized. It must be remembered that wind systems are an intermittent power source competing with the reliability and convenience of utility power. Additional power production irregularities will impair consumer acceptance of wind systems.

Conclusion

The acceptance of small wind systems may very well depend more upon system reliability than on other factors such as performance, aesthetics and even in some cases capital cost. The need for producing cost-effective and reliable wind systems will task designers to come up with suitable choices for materials and fabrication processes.

TABLE I

SEVERE CLIMATIC AND ENVIRONMENTAL OPERATING CONDITIONS

Wind Speed	
Survivability	- Gusts up to 74 m/s (165 mph)
Operating Range	- About 4 to 22 m/s (9-50 mph)
Temperature	- -70°C to 60°C (-94°F to 140°F)
Rain	- Torrential downpour w/Hurricane Winds
Icing	- Up to 60 mm (2½ in.) on Surfaces of Rotor, Nacelle, Tower
Atmosphere	- Salt water spray, Heavy Industrial Pollution
Hail	- Impact by 40 mm (1½ in.) Golf Ball Hail
Lightning	- Direct strikes without causing Major Damage
Airborne Particulates	- Sand and Dust storms

Figure 1
 PARTS OF A TYPICAL HORIZONTAL-AXIS WIND SYSTEM (DOWNWIND ROTOR)
 (Not to Scale)

FRETTING AND FATIGUE IN WIND ENERGY SYSTEMS

by

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INTRODUCTION

The successful design of a wind energy system must take into account the fretting and fatigue resistance of the materials utilized. In order to illustrate the nature of the design procedure and the types of materials involved, a particular example will be used, namely the 150 foot wind turbine blades designed and fabricated by The Kaman Aerospace Corporation for the NASA Lewis Research Center. Figure 1 indicates the scale of these blades which weigh approximately 36,000 lbs, of which 26,000 lbs are composite structure and the rest the steel adapter from blade to hub. This blade was designed and fabricated using state-of-the-art procedures, and is the largest blade fabricated to date. The size itself was selected by NASA as the optimum for a given power output at a given wind velocity. It may be of interest to note that the tip speed at 20 rpm approaches 400 mph.

THE WIND ENERGY SYSTEM^(1,2)

The Lewis Laboratory specified that the blade be a series 23000 air foil of 150 ft. radius and of one piece construction (i.e., a blade without a mid-span joint). The rated power for the two-blade system was to be 1800 kw in an 18 mph wind. A downwind rotor, rigid hub, and of particular interest, a 30 year design life were also specified. The pitch of the blades is adjustable with change in wind velocity, but is not varied in each cycle as in the case of a helicopter blade. These and other requirements led to the blade design shown in Fig. 2.

BLADE FABRICATION

The blade is an all-composite construction, with a leading edge blade spar of a filament wound E-glass/epoxy composite in which 90% of the structural fibers are oriented nearly parallel to the longitudinal axis of the blade. In this as well as other wind energy machines, cost is a primary consideration. Therefore a well characterized, low temperature curing epoxy resin system was selected for spar fabrication to avoid the cost of a large high-temperature oven for the 150 ft. blade. The spar has a three-dimensional taper which makes it necessary to reduce the distribution of structural material continuously from root to tip. Local reinforcement is provided at the blade root by interleaving $\pm 45^\circ$ glass cloth between layers of the essentially unidirectional material to achieve an isotropic structure for attachment of the root and adaptor.

The hub adaptor itself is built of ASTM A36 steel (36 ksi yield strength). The hub is a welded box structure and the materials used include A36, A516, A517, and A553 steels at yield strength levels up to 150 ksi. The main bearing for blade rotation is a three row ball bearing which provides for axial alignment as well as thrust loading. Pitch change bearings are also incorporated into the hub assembly. A main thrust bearing allows for tower rotation with change in wind velocity. Some wear of the thrust and three-row ball bearings is anticipated during the design lifetime.

FATIGUE DESIGN

Load analyses were conducted by Kaman for five operating conditions to determine which were critical for fatigue design. Among the operating conditions, Table 1, the gust condition, case 2, produces the highest fatigue loads, and since these gusts are frequently repeated, this condition is critical to infinite life (30 year) design. The bending moments associated with this fatigue critical case 2, primarily due to gust loading, are shown in Fig. 3. The corresponding bending

stresses are shown in Fig. 4. The fatigue resistance of material coupons and of structural models was determined under appropriate mean stress and environmental conditions. Fig. 5 shows the type of results obtained together with the mean $\pm 3\sigma$ curves. Note that all the points plotted represent test suspension, either as the result of attaining a predetermined acceptable number of cycles, or because the specimens developed failures outside the test section. It is seen that the fatigue resistance meets the requirement that the fatigue strength at 10^7 cycles when reduced by three standard deviations (3σ) should exceed ± 6000 psi. For comparison, it is noted that the ultimate tensile strength of the spar should exceed 50,000 psi. The stress distribution around bolt holes in the blade root attachment area under normal operating conditions, case 1, is shown in Fig. 6, and here also the stress levels are below the design allowables.

FRETTING

Relative micromotion between contacting parts of a wind energy system can lead to fretting and the initiation of a fatigue crack. Whether or not fretting will be a problem is not clear at this early date and will need actual service experience for assessment. It is somewhat reassuring that fretting between fiberglass components does not appear to be as serious as between metal components because of a greater difficulty in initiating fatigue cracks. In addition, procedures common to the helicopter industry to reduce fretting have been incorporated into the 150 ft. blade design.

An example of an area designed with fretting in mind is the bolt circle which connects the blade to the hub adaptor. This circle consists of 18 3-inch bolts of 4340 steel heat-treated to an 180 ksi yield strength level. Tin-cadmium plating on the bolts acts as a good dry lubricant as well as a corrosion inhibitor. In addition, the clamping pressures are specified to minimize relative motion in the vicinity of the stress raisers and to allow much of the relative motion to take place in regions of lower stress where there is less likelihood of initiation of

a fatigue crack. Steel bushings having a 5-inch outer diameter are installed in the spar composite to accept the bolts, and the joint was designed and fabricated to achieve not only uniform load sharing between fasteners but also acceptable low stresses in the composite.

Other measures which can be taken to minimize fretting fatigue include shot peening or burnishing of bolt holes, the use of sacrificial liners, and the use of electroplated silver and diffused nickel cadmium coatings on steel inserts. Fretting in threaded areas can be minimized through attention to thread design and by the use of a different fastener or attachment.^(3,4) Of course attention to surface finish and the drilling, reaming and deburring of holes are routine practical considerations. In certain cases, teflon or molybdate solid film lubricants may also prove to be beneficial.

In the 150-foot blade system, the pitch-change roller bearings are also of concern since they are in use only intermittently. System vibration during off-use periods may result in the type of fretting known as false brinnelling and consequent impairment of bearing performance.

CONCLUSIONS

In summary, there appears to be no fatigue or fretting problems unique to the wind energy system described, particularly since state-of-the-art methodology is used and previous experience with similar components in the helicopter industry has been utilized in the design. However, even with the benefit of this technology transfer, the 30 year design (2×10^8 cycles) under exposure to all sorts of weather variations is certainly a stringent requirement. Should fatigue or fretting problems develop they will be made evident through impairment of system performance due to loss of blade stiffness or difficulty in bearing operation. A regular schedule of inspection and preventive maintenance will serve to detect or prevent such damage before it reaches such a critical stage that extensive shutdown and repair would be required. However, since price per kilowatt-hour is the overriding consideration, the real challenge is to design and build wind energy systems which are free of fatigue and fretting fatigue at minimum cost.

ACKNOWLEDGEMENT

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4. D. W. Lum and J. J. Crosby, *ibid.*, p. 651.

TABLE I. OPERATING CHARACTERISTICS FOR ROTATING CONDITIONS

CASE NO.	VELOCITY	RPM	PITCH ANGLE	THRUST/BLADE	KW/BLADE	YAW ANGLE
1*	18 MPH	16	- 5°	21,560 LBS	910	0
2	60 MPH	20	- 5°	71,170 LBS	2320	0
3	18 MPH	(--VARIABLE DUE TO BLADE FEATHERING--)				0
4	0 MPH	16	- 5°	-11,580 LBS	- 74	0
5	50 MPH	16	- 26.5°	10,770 LBS	900	20°

* Case 1 represents rated power, rpm and velocity conditions.

Figure 1. Photograph of the Kaman 150 ft. Wind Turbine Blade.

Figure 2. 150 Foot Wind Turbine Blade

Case 2: Gust to 60 mph @ Rated Pitch Angle and 20 rpm

Figure 3. 150 Ft Wind Turbine Blade Bending Moments.

Case 2 Critical Fatigue Condition

Figure 4. Fatigue Condition Stresses (Gust + Overspeed).

Figure 5. Spar Material Fatigue Characterization.

Figure 6. Cyclic Radial Bearing and Tangential Stresses for Case 1 - Normal Fatigue Condition.

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GRAPHITE-ALUMINUM COMPOSITE TECHNOLOGY

by

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ABSTRACT

At present, fiber-reinforced-epoxy composites, having a 25- year developmental lead on fiber-reinforced metal matrix composites, have excellent properties for ambient-temperature applications in environments of limited severity. While metal matrix-composites technology is just emerging from infancy, there is nevertheless a broad and deep background of experience, problem solving and application in working with metals per se. These considerations indicate the need to look at the potential advantages of fiber-reinforced aluminum composites, and to survey the rapid advances during the past few years in manufacturing technology. Spin-offs from the non-metals composite technology permit braided and woven graphite fibers to be consolidated into matte, felt, and rigid three-dimensional structures and infiltrated in place. Because the liquid metal infiltration process is essentially a continuous process the potential exists for structural forms to be fabricated directly from woven or braided graphite preforms. Direct infiltration of matte, pressed fiber, and woven graphite fabric has already been investigated, and the foundation exists for rapid expansion of the technology to meet future known and unknown requirements.

INTRODUCTION

Current and Future Materials Requirements: An Overview

Conventional and advanced fiber-reinforced-nonmetal composites are, at present, highly competitive with metal-matrix composites (MMCs) from the standpoints of design, confidence, and cost. The specific properties of tensile stress and elastic modulus of certain fiber-reinforced epoxy composites are extremely high and can be easily utilized in applications in which ambient temperatures prevail and in environments of limited severity. Not only are the graphite-epoxy materials used in aerospace applications, they have come into wide use in consumer applications because of their reliability, their low cost, and their predictability, in addition to their unique properties. This is to be expected. Graphite-epoxy composites development got underway some 25 years ago with the appearance of Fiberglas-reinforced plastics and boron-filament reinforcement. The composites that evolved from these early materials can now be considered to be advanced composites.

Metal-matrix-composite technology is presently at a point that is comparable to the early 1960s development of nonmetals composites. It is in its infancy, but it is rapidly emerging from that stage and deserves attention as complementary technology. The fact of its being complementary is of great importance. Metal-matrix-composite technology is an offshoot of the same development that produced graphite-epoxy composites and in the future, may very well carry composites into applications not feasible for plastics.

Another very important consideration has also to do with environment; particularly with what we don't yet know. This is the matter of environmental hazards. What is known is the problem of electrical interference from graphite fibers that are released into the atmosphere. Electrical interference problems are pervasive and difficult to overcome and not much test data exist. The more graphite-reinforced-composite use expands, the more severe will be the problems.

A new and unexplored class of problems, furthermore, may come into existence; for example, health problems caused by long-term inhalation of hard-to-detect particles of graphite. The manufacturing industry, which is only now being called to public accountability on environmental contamination and health-risk problems, cannot afford to overlook such matters. Here is an area in which graphite-aluminum composites have a definite edge. Graphite-epoxy materials, when they burn, lose their graphite particles to the atmosphere. This is not a problem with aluminum-matrix composites since high temperatures do not ignite them. High temperatures melt them only, and the aluminum matrix remains, retaining the graphite particles within itself. From this aspect alone--environmental hazards and health risks--the aluminum-matrix composites offer significant advantages in future applications.

Finally, there is a broader, deeper base of experience with the metal alloys used in metal-matrix composites than there is in epoxy composites, simply because metal technology has been around a very long time. Experience with problem solving, applications and metalworking is extensive, and thus there is a high level of confidence in metal-matrix alloys. This level of confidence is extremely important because the few years are going to bring into being new and startling materials demands for technologies that are currently in the idea or exploratory stages. As a result of directed development, these new technologies will be appearing on the scene fully developed in five to ten years. Computer and robotic control of manufacturing processes will remove the environmental limitations associated with human control. Thus, new sets of conditions and materials requirements will come into existence. It is particularly with regard to these near-term-future materials requirements that metal-matrix composites may become the materials of choice.

Current Development of Metal-Matrix Composites

The graphite-aluminum system relies on a continuous-casting, liquid-metal infiltration technique pioneered by the Aerospace Corporation, refined by Fiber Materials, Inc., and made available commercial by Material Concepts, Inc. The process involves a chemical vapor deposition (CVD) coating operation that deposits a thin layer of titanium and boron onto multifilament graphite-fiber tows by the reduction of titanium tetrachloride and boron trichloride with metallic zinc vapor. This thin coating, less than 200 Angstroms thick, activates

the surfaces of the graphite fibers to permit wetting by reaction metals such as aluminum and its alloys. Wetting is essential in bringing about the required synergistic response for bonding between the graphite fibers and the metal and also minimizes fiber degradation by the metal during infiltration.

Graphite-aluminum composites have certain economic advantages including materials availability, the low cost of the matrix, the potential low cost of fibers, ease of fabrication, and the potential low cost of manufacturing¹. Graphite yarns have been under development for many years by various domestic and foreign vendors. The impetus for this development has been primarily in the nonmetals composite market; for example, the graphite-reinforced epoxys. Thus, a highly competitive marketplace insures continued product improvement at a lower cost. This factor is important for emerging systems, such as the graphite-aluminum system, in that the potential customers are assured of multiple domestic sources of quality fibers that are made from nonstrategic materials. There is an indirect benefit in having an active commercial interest in graphite fibers, since the impetus of this interest further insures lower costs, defrayed development cost, and capital investment by the civilian economy, all of which assures future materials availability. Likewise, the aluminum matrix is relatively low priced and readily available. The potential exists for overall low cost of manufacturing graphite-aluminum composites because the process is actually a continuous-casting operation. Casting, since it is one of the lowest cost metalworking processes available, offers excellent potential for lowering the graphite-aluminum production costs.

GRAPHITE-ALUMINUM COMPOSITES

Graphite-Aluminum Properties

Graphite-aluminum composites offer several unique properties to the materials user, among which are high specific property values, dimensional stability at high temperatures, excellent low- and high-temperature fatigue strength², excellent machinability, low coefficient of friction³, and excellent wear resistance, retention of ambient temperature mechanical properties at high temperatures⁴, as well as good thermal and electrical conductivity, and ease of bonding and joining. Typical comparisons of tensile stress, σ , with density, ρ (σ/ρ), for graphite-aluminum and Ti-6-4 are as follows: σ/ρ for graphite-aluminum is 1.7×10^6 inches and σ/ρ for Ti-6-4 is 0.96×10^6 inches. Likewise, the ratio of elastic modulus, E , and

density, ρ (E/c), for graphite-aluminum is in the range of 3.0 to 4.0×10^6 inches, while that of Ti-6-4 is 1.025×10^8 inches. Thus in applications where high strength-to-weight and high stiffness-to-weight ratios are important, graphite-aluminum may have the competitive edge over a standard structural alloy.

The fatigue properties of graphite-aluminum composites are excellent. Recent work reported at the Aerospace Corporation² indicates that fatigue-strength ratios (the fatigue strength at 10^7 cycles divided by the tensile strength) for graphite-aluminum composites are typically between 0.7 and 1.0. This compares most favorably with typical fatigue ratios of 0.57 reported for the well-characterized boron-aluminum composites⁵. The fatigue properties of all fiber-reinforced metal-matrix composites depend on how uniformly the fibers are dispersed in the matrix, fabrication conditions, and the inherent properties of the matrix alloy. This excellent fatigue life could be extremely important in government and commercial applications. Graphite-aluminum composites possess excellent machinability. In terms of system costs, this factor could play a significant role, since conventional tooling used to machine aluminum can be used in working graphite-aluminum composites.

Certain applications of graphite-aluminum composites could involve requirements in which low coefficient of friction and excellent wear resistance are important. Theoretically, frictional or tribological properties of graphite-aluminum composites can be tailored to meet given requirements. Both the selection and the orientation of the graphite fiber will change the tribological response of the composite. In wear and friction tests, rayon-based Thornel-50 - aluminum composites typically displayed half as much friction and significantly greater wear rates as composites fabricated from PAN-precursor fibers. Wear rates of the aluminums reinforced with PAN-graphite fibers are superior to those of the aluminum matrix itself.

The retention of ambient-temperature mechanical properties at elevated (700 F) temperatures has been demonstrated for graphite-aluminum composites. Harriqan, et al.⁴, have shown that graphite-aluminum composites retain 70 percent of their room-temperature tensile strength to temperatures within 50 C of the melting point of the aluminum matrix. Likewise, creep resistance is excellent at temperatures within 100 C of the melting temperature of the aluminum matrix.

Limited corrosion studies with various graphite-alumi-

num composites indicates that corrosion rates in 3.5 percent NaCl solutions were about the same as, or slightly higher than, the corrosion rates of the matrix alloy itself⁶. Certainly there is evidence that processing conditions influence corrosion behavior of graphite-aluminum composites.

As indicated in the table below, translation of fiber properties of commercially available precursor wire is excellent. Mechanical properties typically equal or excel Rule-of-Mixture (ROM) predictions. The properties of the pitch-based precursor wire are included because of the great potential of the pitch-based graphite fiber. In all experimental cases, the pitch fiber demonstrated remarkably good translation of properties to the precursor-wire composite, as well as to the plates made by a secondary fabrication process, such as diffusion bonding. Although the pitch-based fiber used for these studies had a tensile strength of 175 ksi and a modulus of 55×10^6 psi, the vendor, Union Carbide, has demonstrated that it possesses significantly greater tensile strengths on a research and development basis. The promise of improved properties together with the lower cost of this material makes it an excellent candidate for graphite-aluminum composites.

PROPERTIES OF GRAPHITE-ALUMINUM PRECURSOR WIRE

Wire	Fiber Volume Percent	Tensile Stress, σ , ksi	Elastic Modulus, E , psi $\times 10^6$
T-50 - A201	32	95 - 100	20
HM-A201(a)	35 - 40	135 - 145	24
GY70-A201 (a)	35 - 40	135 - 140	32
Thornel-pitch(a)	35 - 40	68 - 76	20
VSB32	35 - 40	90 - 110	20
VSB34	35 - 40	135 - 150	25

(a) Sullivan, Pamela, Nevada Engineering and Testing Company, Long Beach, California. Personal Communication, September, 1977.

Processing of Graphite-Aluminum Composites

Available Processes

There are several processes available for fabrica-

ting graphite-aluminum composites, including electroplating the graphite fiber with nickel, vapor deposition of nickel onto the graphite fiber, activation of the graphite fiber by sodium infiltration, and coating the graphite fiber with titanium-boron. In each process, the surface of the graphite is coated with a material that promotes wetting when the fiber is further processed in an aluminum matrix. Typically, the nickel-coated fibers are diffusion bonded between foils of aluminum, while the sodium activation and the titanium-boron-coated fibers are processed through molten aluminum to form a precursor wire. This paper focuses on the liquid-metal infiltration process that employs the titanium-boron-coating method.

Liquid-Metal Infiltration

The liquid-metal infiltration process demonstrates that each individual fiber can be coated. The complete coating of each fiber within a fiber tow is necessary to promote the wetting required for proper fiber-matrix bonding, and it is the quality of the fiber-matrix bonding that insures the synergistic response required for full translation of fiber properties. The process is amenable to infiltrating many forms of graphite fiber because it is, in essence, a casting process. The process can either be continuous or batch in situ, depending upon the form of the graphite fiber, such as continuous fiber tows or discrete woven shapes, that is employed. Results show that the liquid metal infiltrates the graphite tows or shapes well, with no evidence of microcracking in the matrix, and that fiber distributions are fairly uniform.

The versatility of the molten-metal infiltration method of producing graphite-aluminum precursor wire is being extended to other useful metal-composite systems. To date, graphite-lead, graphite-copper, and graphite-magnesium have been successfully infiltrated utilizing the same varieties of yarn as are typically used with graphite-aluminum⁷

Manufacturing Technology

The rayon-based Thornel-50 (T-50) was used with considerable success to demonstrate the producibility of T-50 - aluminum precursor wire. The technology scale-up was successfully employed under a Manufacturing Technology Program⁸. This program essentially increased the speed of the fiber coating

and infiltration process three- to fourfold; it introduced textile techniques for feeding the graphite T-50 yarns into the CVD chamber; it simplified the process and lowered the cost of the graphite-aluminum precursor wire by 33 percent. This process. This process employed a yarn-croel design that permitted the direct insertion of vendor's yarn spools into the apparatus, thereby cutting down on the excessive handling of yarns that was typical of the earlier method. This excessive yarn handling caused fiber degradation and yarn fraying. In the earlier method, the yarns were rewound on metallic spools, heat treated to remove the polyvinyl (PVA) sizing, and inserted into an inert-gas-filled chamber for introduction into the process. This procedure did not permit either changing the yarns or varying the number of yarn tows, and it made repair of yarn breaks difficult.

The most recent advance in producing precursor composite wire employs a multichambered, multilined CVD unit developed under a Navy Manufacturing Technology Program⁹. The primary thrust of this program is to demonstrate a production capability of 2000 pounds per year of precursor wire using Union Carbide's VSB32 pitch fibers and Celanese's GY70 high-modulus polyacrylonitrile (PAN) -based fibers. Specific improvements in such unit operations as yarn transport, CVD chambers, melt capacity, and reactant-gas monitoring are among the chief improvements for this system. The four-line capacity increases production fourfold, while the aforementioned unit operations improvements increased the yield of the precursor wire.

The graphite yarns as supplied by the vendor usually are coated with a sizing or an epoxy-compatible resin for handleability and ease of bonding to nonmetals. Although this is a requirement for the nonmetals applications, the PVA is not required in the titanium-boron CVD process. Therefore, the PVA in-line furnace removes the PVA coating as part of the continuous-production operations. Next, the yarn is passed through a precoat furnace that serves to clean or activate the yarn surface. The activated yarn is then passed through a gas trap into the CVD furnace where the titanium-boron coating is deposited on the yarn. The yarn is then drawn through a molten-metal bath and emerges as precursor wire. The T-50, eight-strand precursor wire is approximately 0.050 inch in diameter.

Typically, this wire can be single-strand, three-strand, five-strand, eight-strand, or as much as sixteen

strands, depending on the user's requirements. Current emphasis is on polyacrylonitrile (PAN) and pitch-based fibers, and this emphasis is expected to continue. The PAN fibers presently market for 15 to 50 percent of the base cost of the rayon-based T-50, while the Thornel-pitch fibers sell for approximately 8 percent of the T-50 cost.

The precursor wire can be formed into many useful structural shapes by the usual metal-forming processes. Innovative cross-plying employed with interleaving diffusion-bonding techniques have enabled fabricators to advance significantly the state of the art of fabricating graphite-aluminum composites into useful configurations. Hot isostatic pressing can be used to form structural shapes directly from precursor wire. Similarly, several conventional metalworking processes, such as pultrusion and extrusion, have been demonstrated as viable techniques to form graphite-aluminum composite tubes, rods, and bars.

Future Technology

As shown below in the table, there is a logical extension of the liquid-metal infiltration technology into new product forms. Although preliminary feasibility for this extension of the technology into woven preforms and discontinuous felted-fiber shapes has been demonstrated, considerable effort remains in optimizing each process, defining limitations, and making the transition to a viable production process.

POTENTIAL GRAPHITE-ALUMINUM PRODUCTS PREPARED BY LIQUID-METAL INFILTRATION

Product	Fiber Form	Infiltration Mode
Prepreg Wire	Continuous	Continuous
Tape	Continuous (1-D)	Continuous
Sheet	Continuous (2-D weave)	Continuous
Shapes	Continuous (3-D weave)	<u>In situ</u>
Ingots and Shapes	Discontinuous Carbon sintered	<u>In situ</u>

Woven Preforms

An exciting possibility currently being explored with graphite-aluminum composites involves the use of preforms. Non-metal technologists have utilized preforms remarkably well in the shapes of prepreg tapes, cloths, braided forms, and multi-dimensional woven preforms. Feasibility of producing tapes by the molten-infiltration process from woven preforms has been established¹⁰. One- and 3-inch-wide woven tapes (2-D) have been infiltrated. These 2-D orthogonally woven materials, being less anisotropic than unidirectional 1-D tapes, can offer significant structural improvement without cross plying of precursor wire.

The tapes are in the as-cast condition and need to be straightened or creep formed into desired shapes. The straightening operation could be accomplished either as an additional in-line step or as a separate operation. Metallographic examination of the 2-D infiltrated tapes reveals good infiltration, minimal porosity, and little evidence of micro-cracking.

Another technology spin-off from the nonmetallics industry is the braiding or weaving technology, which permits the formation of woven shapes with graphite fibers. This technology can be directly applied to graphite-aluminum composites. The braided or woven green shapes can be subjected to the CVD coating operation and infiltrated with molten aluminum. Thus, the continuous casting of graphite-aluminum tubes using braided or woven preforms could be feasible. Likewise, the 3-D carbon-carbon weaving technology developed for the reentry vehicle and for rocket-nozzle applications could be borrowed for processing graphite-aluminum 3-D reinforced shapes. This spin-off would permit preforms to be made to near-net shape, carbon sintered to maintain green strength, and infiltrated in situ (batch operation). These forms could be custom designed with greater reinforcements in the principal stress directions, thus offering the designer unlimited freedom of configuration.

The point to be emphasized here is that the braiding and 3-D technology investment, in terms of both hardware and experience, are currently available. Thus, they require no major investment on the part of potential graphite-aluminum users.

Felted Preforms

Spin-off from the highly developed technologies of papermaking and feltmaking could provide yet another type of graphite-aluminum composite. The adaptation of these technologies would employ the highly desirable pitch staple fibers. Feasibility of infiltrating pitch matte has been established⁹. Green felted shapes could be carbon sintered to permit handling and shape retention during the infiltration process. Typical microstructure of infiltrated pitch matte reveals excellent wetting, good fiber distribution, and absence of microcracking. The economic advantage of such configurations is great. Pitch fiber has the greatest potential of lowest-cost reinforcement while offering highly desirable properties.

Future Trends and Applications

While the current state of the art of graphite-aluminum is focused on the precursor wire, the next generation of graphite-aluminum composites will emphasize the 1-D-wide tows as well as the 2-D sheets. In the early 1980s the 3-D technology should become the current state of the art.

The capability of direct fabrication of near-net shapes that minimize machining and secondary fabrication processes could result in a significant advantage for the employment of graphite-aluminum metal-matrix composites in future systems applications.

Typical military applications of graphite-aluminum composites, based on their desirable properties, might be space antennas, engine components, advanced space-shuttle structures, aircraft improvements, missile components (tactical and strategic), launch vehicle and satellite structural materials, deep-submergence structures, torpedoes, hydrofoils, helicopter rotor blades and transmission cases, weapons components, and electrical machinery components. Another potential application would be reinforced light-weight, high-strength, large-caliber gun tubes.

The usefulness and adaptability of the graphite-aluminum system indicates its potential range of application: the ease with which the titanium-boron liquid-infiltration process lends itself to continuous and batch operations, the fact

that it can be used with most commercially available graphite fibers and most aluminum alloys, is adaptable to use with pultruded tows, wide tows, 2-D woven sheets, 3-D woven preforms, rolled forms, and can also be employed in conjunction with several conventional metalworking processes; all these factors demonstrate the versatility of the graphite-aluminum system.

ACKNOWLEDGEMENTS

The authors express their gratitude to the Naval Sea Systems Command for their continued support of the graphite-aluminum technology. Much of the discussion of manufacturing technology and the woven infiltrated tapes was based on work performed under Contract No. N00197-76-C-0065, "Development of a Production Process for Graphite-Aluminum Wire", for the Naval Ordnance Station, Louisville, Kentucky, and under Contract No. N6091-76-0173, "Feasibility of Utilizing the Liquid-Metal Infiltration Process for the Fabrication of Bulk Aluminum-Graphite Composite Materials", for the Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland.

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LOAD-ENVIRONMENT INTERACTIONS IN FATIGUE CRACK GROWTH

by

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Background

Components of wind energy collectors, such as blades for horizontal-axis wind turbines, can accumulate well over 10 million cycles of fatigue loads each year. The actual numbers of fatigue load cycles would depend on the operating speed and the extent of utilization. Metal fatigue, therefore, is one of the significant factors to be considered in the design of wind energy collection systems to ensure reliable operation. Fracture mechanics technology that is now used widely in the aerospace industry can be applied directly to assist in the design and selection of materials for wind energy collection systems. This technology is used to assess the growth of cracks that might be present in a structural component or that might initiate early in the life of such a component, and to determine its residual strength. The reliability of the assessment depends, to a large extent, on a clear appreciation of potential load-environment interactions in fatigue crack growth in the acquisition and utilization of material characterization data.

Load-Environment Interactions

Because of the very large numbers of load cycles and the relatively low operating speeds involved in wind energy collectors, fatigue crack growth in the very low rate region (that is, in the so-called threshold region with growth rates ranging from about 10^{-12} to 10^{-8} m/cycle) at low frequencies (approximately 1 Hz) is of primary interest. Data in this region are extremely limited, and environment-load interactions have not been fully recognized and explored.

Because of time and cost constraints, most of these data have been obtained at relatively high frequencies (i.e., greater than 10 Hz). Experience with fatigue crack growth in the high growth rate region (greater than 10^{-9}

m/cycle) suggests that frequency can have a pronounced influence on the rate of fatigue crack growth. This influence is a reflection of load-environment interactions, and depends on the reactivity of the material with the particular environment, temperature, etc. In addition, load ratio or mean load is expected to have a significant effect on fatigue crack growth, particularly at the very low growth rates. This effect can also depend on both thermal and chemical environments. Understanding of load-environment interactions is beginning to be developed. It is not at a stage, however, where reliable predictions can be made. This understanding is needed for the development of quantitative predictive tools, and to provide guidance for the design and operation of wind energy collection systems. Recognition of the potential effects of load-environment interactions, in the mean time, would go a long way towards avoiding costly problems at a later date.

Research/Engineering Needs

Reliability of wind energy collection systems, like other engineering systems, depends on cooperation between the materials and design community. From the materials point of view, some of the research/engineering needs are as follows:

- 0 Proper characterization of materials to reflect realistic operating conditions. In this regard, accelerated testing should be avoided unless adequate correlation between test and operational conditions can be established.
- 0 Develop fundamental understanding of load-environment interactions, as well as that of the mechanism for fatigue, so that models for predicting fatigue crack growth response under the conjoint actions of applied stress and (chemical and thermal) environments can be established.
- 0 Utilize existing information and understanding to provide guidelines for extrapolation of design data and for development of accelerated tests.

Monitoring and Performance Evaluation

A CORROSION PROTECTION MONITOR FOR AUTOMOTIVE COOLING SYSTEMS AND
LIQUID HEAT TRANSFER SYSTEMS

by

R. Baboian

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Attleboro, Massachusetts

A CORROSION PROTECTION MONITOR
FOR AUTOMOTIVE COOLING SYSTEMS AND
OTHER LIQUID HEAT TRANSFER SYSTEMS

INTRODUCTION

Corrosion problems in automobile engine cooling systems are well known by the automotive engineer and consumer alike. Both water and antifreeze (ethylene glycol) corrode the engine, radiator, and associated parts. As a result, corrosion inhibitors are added to the antifreeze solution. Unfortunately, the process does not end there, for these inhibitors break down under heat, flow and pressure. When that happens, the solution begins to attack the engine and radiator, causing pitting, cavitation and other forms of corrosion even though the antifreeze characteristics are maintained.

The problem has been in knowing when the inhibitors break down so that corrective steps can be taken. This brochure describes how a small electronic sensor made by Texas Instruments solves that problem.

Although the sensor was developed originally for the automobile, and can now best be explained in terms of an automotive cooling system, it is by no means limited to automobiles. The sensor was designed to detect corrosion in water-based heat transfer fluids that use ethylene glycol or a like chemical along with corrosion inhibitors. Such systems are also used in connection with solar and thermal energy, in machine tools, presses, die-casting machines and in many other kinds of production and processing equipment.

Corrosion and Ethylene Glycol

Since most automobile engines are cast iron and water-cooled, engine metal will immediately start to corrode when exposed to plain tap water. This corrosion is accelerated by the high operating temperatures of the engine, the flow characteristics, and the presence of trace elements such as chlorides in most tap waters.

Many years ago it was discovered that ethylene glycol would stop engine coolant from freezing. This additive became generically known as antifreeze, and is highly effective. It also becomes highly corrosive with time due to thermal degradation. As this fact became known, chemicals were added to antifreeze to act as corrosion inhibitors. The inhibitors form a protective film on engine walls that retards corrosion much as a corrosion-retarding oxide film on stainless steels. Unfortunately, the inhibitor breaks down under heat and pressure, leaving engine walls exposed and once again the ethylene glycol solution will attack the metal. This process of inhibitor breakdown is shown in Figure 1.

Clearly, if it were possible to monitor inhibitor breakdown and identify Stage B in Figure 1, it would also be possible to forestall corrosion beyond the life of the car simply by adding more antifreeze (inhibitor). But making that identification has proven to be a difficult problem.

The promise of a solution to this problem lies in the development of a corrosion monitor for the cooling system.

FIGURE 1

The Corrosivity Monitor

Corrosion is an electrochemical phenomenon. Engineers reasoned that to monitor corrosion it would be necessary to measure one or more of its electrical properties -- voltage, current, resistivity, etc. A number of monitors were designed and tested. They all shared a common method and a common failing. In one way or another, each employed the principle of the closed circuit, in which a voltage would be impressed through the solution in order to measure the current or other electrical phenomena of the solution. When the current varied by a certain amount, it was further reasoned, the point of corrosion could be identified. In theory this was correct. In practice it did not work because the external voltage itself altered (polarized) the measuring system, a factor that made accurate measurement of the critical data difficult and uneconomical.

Rethinking the Corrosivity Monitor Problem

In electrochemistry there is a phenomenon called static solution potential. For our purposes, this refers to the "voltage" at the interface where metal meets solution.

Dr. Robert Baboian and Gardner Haynes of the Texas Instruments Electrochemical and Corrosion Laboratory had an idea that it should be possible to measure this static solution potential with an electronic sensor. If the solution potential varied when the liquid became corrosive, and if these changes could be accurately measured against a reference potential, might not it be possible to invent an alarm system that would signal when the changes were taking place? They thought it would. But first they had to establish parameters for the behavior, as expressed electrochemically, of inhibited ethylene glycol under typical engine operating conditions. The results of this work can be seen in the following chart.

FIGURE 2

*SUBJECTED TO PERIODIC HIGH TEMPERATURES,
AS UNDER NORMAL DRIVING CONDITIONS

A Monitor That Works

To monitor the variances in solution potential, it was necessary to invent a new economical way of doing it, without repeating the mistakes of the past. The answer came out of solid-state electronics, and, like so many successful inventions, it looks disarmingly simple. The sensor consists of a probe and an electronic circuit which interprets the probe output and displays the results.

The probe itself is about the size of a penlight battery and has two electrodes, one a sensing electrode, the other a reference electrode. TI tests show that the solution potential that occurs between these two electrodes directly correlates with the corrosive behavior of the fluid as is shown in Figure 3.

FIGURE 3

LABORATORY COOLANT CORROSIVITY MEASUREMENTS

The electronic circuit can be set at any particular voltage level, such as 0.3 volts, the level of insipient corrosivity in a coolant solution. When the 0.3 volt level has been reached, the electronic circuit turns on an alarm mechanism. Antifreeze (inhibitor) should be added to the coolant at this time to prevent corrosion. The sensitivity of the device can be varied by changing the voltage at which the alarm is triggered.

The method of indicating when corrosivity has begun can be as varied as the situation demands. The circuit package simply sends out an electronic impulse to the alarm mechanism. In the case of an automobile, the impulse most likely will trigger a buzzer or a light on the dashboard,

a signal to the driver that it is time to add more inhibited antifreeze.

Corrosion Protection for Aluminum

With the mounting pressure on the auto industry to reduce the weight of cars and increase gasoline mileage, automotive designers are using more aluminum. One of the problems with aluminum is that it is highly susceptible to corrosion, so much so that in the past it has usually been rejected as a replacement for car radiators. The TI sensor puts aluminum back in the running.

A full cycle of tests has been conducted on various corrosive solutions in an aluminum environment. It was found that differing concentrations of phosphate and chloride in the coolant affected the point where aluminum corrodes. Aluminum's behavior under corrosive conditions was also known to be much more volatile than conventional automotive metals. The tests indicated that by adding another element to the sensing system, the sensor will work just as well with aluminum as it does with copper, solder, or cast iron. The test results of the modified aluminum sensor in varying concentrations of chloride and phosphate are shown in the following chart.

Other Tests, Other Applications

We have described the sensor as it works in an automobile cooling system. Interest in the sensor has come from many quarters outside the automotive industry and suggests that people in many industries see potential application for the sensor in all sorts of heat-transfer systems.

FIGURE 4

**PERFORMANCE CHARACTERISTICS OF SENSOR
FOR ALUMINUM IN TYPICAL COOLANT***

We are very much aware of this broader potential and have conducted, and continue to conduct, tests on the sensor utilizing a wide variety of solutions and additives that might be found in industrial cooling systems. Work on modification of the sensor is also underway that would make it even more flexible and useful. At this time, however, we feel we have a corrosion sensor system that can be designed to meet the protection requirements of a wide variety of heat-transfer systems.

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SINGLE ION PROPERTY MEASUREMENTS IN HOT WATER

Viewgraphs Presented

by

J. Cobble

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San Diego, California

Single Ion Property Measurements in Hot Water

Conductivity

- Lack of fundamental data
- Weakness of electrolytes
- Materials problems
- Unknown chemistry
- Lack of theoretical models

Electrode Measurements

- Low concentrations
- Reference electrode problems
- H^+/H_2 electrode problems
- Lack of pH standards at high temperatures
- No systematic electrochemistry

Single Ion Property Measurements in Hot Water

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HIGH TEMPERATURE CORROSION FATIGUE

by

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HIGH TEMPERATURE CORROSION FATIGUE

Corrosion fatigue in high temperature aqueous environments can cause crack nucleation and growth in the heat exchangers of steam supply systems. The studies that are described in this presentation were aimed at determining the extent of corrosion fatigue damage that might occur under fully reversed loading in an environment that simulated the departure from nucleate boiling (DNB) region in an LMFBR steam generator. While the materials studied, 2½ Cr-1Mo steel, and the application, LMFBR steam generators were certainly different than those to be used in solar powered steam supply systems, related corrosion fatigue damage may occur in the Incoloy 800 tubes of the collector in the Barstow Tower Power and future solar systems. For this reason the unique experimental facilities and results developed for LMFBR applications can serve as guidelines for required engineering applications for solar systems. The experimental facilities shown and more completely described in Reference 1, linked a button lead tensile sample within a high pressure, high temperature system [1600 psi, 316°C(600°)] to a fatigue facility. Fully reversed tension to compression, strain control corrosion fatigue experiments were conducted in order to determine the effect of the DNB environment on the S/N engineering curve and the alloy endurance limit. Similar data are required for solar systems, namely the effect of internal aqueous environments on the design allowable curve and fatigue life.

The attached figures illustrate some of the experimental methods and results for the LMFBR program.

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Schematic - Corrosion Fatigue Test Facility.

Monotonic and Derived Cyclic Stress-Strain Curves for Isothermal Annealed (Iso-Annealed) Plus Post Weld Heat Treated (PWHT) 2-1/4Cr-1Mo Steel from ESR Heat No. 91775. ORNL Cyclic and Monotonic Curves for 316°C (600°F).

Results of Fully Reversed Cycled Corrosion Fatigue Tests in Deaerated 5% Sodium Hydroxide at 316°C (600°F) for Isothermally Annealed Plus Post Weld Heat Treated (PWHT) 2-1/4Cr-1Mo Steel - Heat No. 91775 - In Reference to Curves Developed in Air and The Design Allowable.

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PH MONITORS FOR HIGH TEMPERATURE
AQUEOUS SOLAR SYSTEMS

by

D. D. Macdonald, A. C. Scott, and P. Wentrcek

SRI International
Menlo Park, California

Presented by

D. D. Macdonald

The long term reliable operation of aqueous heat transport circuits for solar energy systems will require the close monitoring of water chemistry parameters at elevated temperatures. Many of the monitoring techniques currently used in the nuclear power industry will probably be adopted for solar systems. However, the less viable economic base for solar power will dictate construction of the heat transfer circuits from low alloy steels, which are more susceptible to corrosion than the high alloy types such as 304SS that are now used in the nuclear industry. Maintenance of the corrosion rate at an acceptably low level will therefore require the monitoring and control of pH and redox potential in the high temperature environment. Neither of these parameters are currently monitored at elevated temperatures on a regular basis in nuclear or fossil fueled power generating systems.

A research program, funded by the Electric Power Research Institute, is being carried out at SRI International to develop monitors for pH and redox potential for use in aqueous systems at temperatures as high as 275°C. The pH probe is based on the palladium-hydrogen system in which the potential-determining process is considered to be the quasi-equilibrium between palladium hydride and hydrogen ions in solution. In the case of the redox probe, the potential is established at a platinum electrode by the competitive reactions

The potentials of both the pH and redox probes are measured with respect to a pressure balanced external silver-silver chloride electrode. The thermal diffusion potential associated with the external reference electrode has been calibrated for, so that the measured potentials are directly comparable to the SHE scale.

Typical potential versus pH plots for the pH probe are shown in Figure 1 for temperatures of 25°C, 100°C, 200°C, and 275°C. These data were obtained using boric acid-lithium hydroxide buffer solutions, and the pH_T values at each temperature were computed from known values for the dissociation constants for the components. Linear correlations were obtained as demanded by theory. However, the gradients of the lines are less than indicated by the Nernst equation, particularly at elevated temperatures. We have tentatively attributed this phenomenon to irreversible effects associated with the desorption of hydrogen from the lattice. From a practical viewpoint, the potential of the pH probe can be measured to within ± 5 mV therefore yielding a precision of ± 0.06 in pH at 275°C.

A typical redox probe trace on cycling a high temperature boric acid system between oxygen (4.1% in N_2) sparging and hydrogen (10.6% in N_2) sparging is shown in Figure 2. The redox potential is seen to respond rapidly to injection of oxygen into the system but more slowly to the injection of hydrogen. The rapid response to oxygen is desirable since this component is expected to be the most deleterious as far as corrosion is concerned.

Financial support for this work by the Electric Power Research Institute, Palo Alto, California, under Contract RP1168-1 is gratefully acknowledged.

SA-7307-30

FIGURE 1 POTENTIAL-pH RESPONSE OF THE PALLADIUM-HYDRIDE ELECTRODE AS A FUNCTION OF TEMPERATURE

ΔE_{SHE} = Potential with respect to the standard hydrogen electrode at the temperature of interest.

SA-7307-34

FIGURE 2 RESPONSE OF THE REDOX PROBE ON CYCLING BETWEEN 1.05% HYDROGEN → 4.1% OXYGEN
→ 10.6% HYDROGEN

Solution = 0.01M boric acid, T = 275°C.

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GALVANIC CORROSION OF AL ALLOYS
MONITORED BY ACOUSTIC EMISSION

by

F. Mansfeld and P. J. Stocker

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Presented by

F. Mansfeld

Galvanic Corrosion of Al Alloys Monitored by Acoustic Emission

F. Mansfeld* and P. J. Stocker

Science Center, Rockwell International, Thousand Oaks, California 91360

Kettig and Felsen (1) have recently shown that acoustic emission has some promise in monitoring corrosion reactions of unstressed, freely corroding materials and galvanic couples. The data presented were typically taken over a 10 to 30 min. period with emphasis on Al alloys. We have started a program to evaluate the acoustic emission method in more detail, determine the source of the signal monitored and obtain correlations between electrochemical and acoustic data.

The results presented here involve the Al alloys 1100-0 and Al 2024-T851 coupled to Cu (OFHC), 4130 steel, Cd (99.97%) and Zn (99.9%) in aerated 3.5% NaCl. The corrosion behavior of the galvanic couples has been studied in detail earlier (2). The acoustic emission from the sample is detected by a piezoelectric transducer (PZT) which has a peak frequency response in the 150-200 KHz range. Details of the method of counting the individual sound bursts will be described elsewhere (3). The Al alloys were deoxidized in AMCHEM-deoxidizer for 10 min. at 21°C and then immersed in deionized water for one hour. The sample was then immersed in 3.5% NaCl for one hour and the accumulated counts and the corrosion potential ϕ_{corr} monitored on a two-pen strip chart recorder. After one hour the Al alloy was coupled to one of the dissimilar metals and the accumulated counts, the galvanic current measured as described earlier (2) and the potential of the couple ϕ_g monitored for 30 min., after which time the sample was decoupled and acoustic emission and ϕ_{corr} were monitored for an additional 30 min.

Fig. 1 and Table I show the results obtained for Al 2024. The corrosion rates for uncoupled (r_0) and coupled (r_A) Al alloys are from Mansfeld et al (2) for 24 hour tests. The reproducibility of the acoustic emission data was quite satisfactory for the uncoupled

alloy with an average rate of 41 ± 5 counts per min. When the Al alloy was coupled to 4130 steel or Cu a sharp rise occurred. The count rate decreased somewhat after about 5 min. and became constant for the rest of the 30 min. When the dissimilar metal was disconnected, the acoustic emission rate increased for a short time and then decreased again to low values. The data in Table I are average values for the 60 min. or 30 min. time periods. For Al 2024 coupled to Cd acoustic emission was very much reduced with a rate of 0.5 counts/min. When contact to Cd was disconnected, the count rate first increased and then decreased again. This phenomenon was much more pronounced when Al 2024 was coupled to zinc. In this case the count rate decreased somewhat when the zinc was disconnected. The potential of the Al alloy became more positive (Fig. 2) and when it reached a maximum of about -0.61V vs SCE the count rate increased sharply. Presumably, at this potential pitting occurs again. About 10 min. after decoupling the count rate decreased again.

Table I Acoustic Emission from Al Alloys in 3.5% NaCl, 21 $\pm$ 1°C

	Uncoupled 60 min.		Coupled 30 min.		Uncoupled 30 min.
	Counts/ Min.	r_0 (mdd)	Counts/ Min.	r_A (mdd)	Counts/ Min.
Al 2024/Cu	41	5.25	497	64.4	35
Al 2024/Steel	50	3.25	730	11.4	117
Al 2024/Cd	32	5.25	0.5	11.2	97
Al 2024/Zn	42	5.25	50	24.6	385
Al 1100/Cu	1.5	0.24	5200	40.6	1.6
Al 1100/Steel	3.0	0.24	4550	30.4	1.1
Al 1100/Cd	1.1	0.24	1.0	1.5	0.9
Al 1100/Zn	5.0	0.24	3.1	4.5	12

Note: Corrosion rate data r_0 , r_A are from Ref. 2.

Al 1100, which is much more corrosion resistant than Al 2024 in 3.5% NaCl (2), produces only very few counts when freely corroding (3 ± 2 counts/min., Table I). When

*Electrochemical Society Active Member

coupled to Cu or steel the count rate increases tremendously (Table I) reflecting the pronounced increase in dissolution rates due to coupling reported earlier. When coupled to Cd or Zn, on the other hand, the count rate did not increase. When Cu or steel are disconnected from Al 1100, the count rate decreases almost immediately returning to the value found initially for the freely corroding Al 1100.

The origin of the acoustic emission is not clear yet. Our observations on steel and stainless steel in acid media suggest, however, that hydrogen gas generated within the pits in the Al alloy is contributing significantly to the acoustic emission. The present preliminary results suggest that acoustic emission can become a valuable tool for corrosion research and monitoring of corrosion reactions. A comparison of the acoustic emission and corrosion rate data in Table I shows that the acoustic measurements reflect accurately the effect of the dissimilar metal and the different corrosion behavior of the two Al alloys. The results of Fig. 2 seem to give information about the pitting process which could not be followed with electrochemical techniques in the same manner.

ACKNOWLEDGEMENT

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Fig. 1. Acoustic emission from Al 2024 in 3.5% NaCl. One hour uncoupled, 30 min. coupled, 30 min. uncoupled.

Fig. 2. Count rate and potential of Al 2024 coupled to Zn and uncoupled in 3.5% NaCl.

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ACOUSTIC EMISSION FROM CORRODING ELECTRODES

by

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ACOUSTIC EMISSION FROM CORRODING ELECTRODES

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ABSTRACT

Acoustic emission measurements have been performed on unstressed Al alloys which were freely corroding or coupled to Cu, 4130 steel, Cd or Zn in 3.5% NaCl. The rate of acoustic emission is in qualitative agreement with the observed corrosion rates. The acoustic emission is probably a result of hydrogen bubble evolution in the acidified pits. The rate of acoustic emission of 4130 steel in HCl also follows the corrosion behavior, decreasing significantly with addition of organic corrosion inhibitor. Stainless steel type 304 was studied freely corroding or at applied constant anodic or cathodic currents. The highest rates of acoustic emission were determined at cathodic currents; when an anodic current was applied the acoustic emission rate was higher than for a freely corroding sample and showed wide fluctuations which continued for some time when anodic polarization was discontinued. For localized corrosion of Al alloys and stainless steel the acoustic emission process seems to reflect the statistical nature of the pitting process.

INTRODUCTION

A few papers have been published recently which report the use of acoustic emission (AE) measurements for monitoring of corrosion processes. Rettig and Felsen (1) have described simple experiments in which qualitative correlations were observed between AE and corrosion behavior of iron wire in HCl, Al wire in NaCl and Fe/Al galvanic couples in NaCl. Druchenko et al (2) have given a qualitative description of AE generated in metals by stress corrosion cracking, pitting, hydrogen absorption and desorption and electroplating. These authors concluded that "micro-acoustic corrosion processes should become an important corrosion discipline" (2). A program has been started in this laboratory with the aim of evaluating the AE method in more detail, determining the source(s) of the signal monitored and obtaining correlations between electrochemical and micro-acoustic data. Some results obtained until now are being reported here for unstressed Al alloys, steel and stainless steel.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental arrangement for monitoring acoustic emission signals is shown in Fig. 1. A piezoelectric transducer is attached to the top of the sample which is partly immersed in the test solution. The signal from the transducer is fed into a differential amplifier and from there into a high pass filter. In typical experiments a frequency range of 30 kHz to 1 MHz was used. The output of the filter was used to trigger the oscilloscope, the trigger level was set in a manner which excluded white noise, only one event in a 500 μ sec period was counted. In the initial experiments with Al alloys in NaCl only the accumulated AE counts were recorded, in later experiments the rate of AE was also recorded using in most cases 10 sec intervals.

1. Localized Corrosion of Al Alloys in NaCl

The Al alloys 1100-0 and 2024-T851 were freely corroding or were coupled to Cu (OFHC), 4130 steel, Cd (99.97%) and Zn (99.9%) in 3.5% NaCl open to air at $21 \pm 1^\circ\text{C}$ (3). The corrosion behavior of these alloys and galvanic couples had been studied in detail earlier (4).

The Al alloys were deoxidized in AMCHEM-deoxidizer for 10 min. at 21°C and then immersed in deionized water for one hour. The sample was then immersed in 3.5% NaCl for one hour and the accumulated counts and the corrosion potential ϕ_{corr} monitored on a two-pen strip chart recorder. After one hour the Al alloy was coupled to one of the dissimilar metals and the accumulated counts, the galvanic current measured as described earlier (4) and the potential of the couple ϕ_g monitored for 30 min., after which time the sample was decoupled and acoustic emission and ϕ_{corr} were monitored for an additional 30 min.

Figure 2 and Table I show the results obtained for Al 2024. The corrosion rates for uncoupled (r_o) and coupled (r_A) Al alloys are from Mansfeld et al (4) for 24 hour tests. The reproducibility of the acoustic emission data was quite satisfactory for the freely corroding alloy with an average rate of 41 ± 5 counts per min. When the Al alloy was coupled to 4130 steel or Cu a sharp rise occurred. The count rate decreased somewhat after about 5 min. and became constant for the rest of the 30 min. When the dissimilar metal was disconnected, the acoustic emission rate increased for a short time and then decreased again to low values. The data in Table I are average values for the 60 min or 30 min. time

periods. For Al 2024 coupled to Cd acoustic emission was very much reduced with a rate of 0.5 counts/min. When contact to Cd was disconnected, the count rate first increased and then decreased again. This phenomenon was much more pronounced when Al 2024 was coupled to zinc. In this case the count rate decreased somewhat when the zinc was disconnected. The potential of the Al alloy became more positive (Fig. 3) and when it reached a maximum of about $-0.61V$ vs SCE the count rate increased sharply. Presumably, at this potential pitting occurs again. About 10 min. after decoupling the count rate decreased again.

Al 1100 produces only very few counts when freely corroding (3 ± 2 counts/min., Table I). When coupled to Cu or steel the count rate increases tremendously (Fig. 4, Table I) reflecting the pronounced increase in dissolution rates due to coupling reported earlier. When coupled to Cd or Zn, on the other hand, the count rate did not increase. When Cu or steel are disconnected from Al 1100, the count rate decreases almost immediately returning to the value found initially for the freely corroding Al 1100.

Figure 5 shows in more detail the rate of AE as a function of time for Al 1100/Cu in 3.5% NaCl. These results seem to reflect the statistical nature of the pitting process on Al alloys in which the activity of the numerous pits distributed over the entire sample area seems to vary with time. This result suggests that AE measurements are capable to provide more detailed information about pit nucleation and growth phenomena especially when used in combination with electrochemical techniques. Figure 6 shows typical AE bursts obtained during the experiment shown in Fig. 5.

The weight loss data for the Al alloys (4) had shown that coupling of Al 2024 to Cu increased corrosion rates by a factor of 12, while the corrosion rate of Al 1100, which has a low corrosion rate when freely corroding but is highly susceptible to pitting which occurs due to coupling to Cu, increased by a factor of 168 (4). The ratio of this increase of corrosion rates ($168:12 = 14$) is about the same as the ratio of the AE rates ($5533:528 = 10.5$) which suggests that AE measurements can be used to follow the pitting process in Al alloys. The origin of the AE signal has not been determined, but it is likely that hydrogen evolution in the acidified pits produces the observed acoustic emission signals. Further support for this explanation is derived from the experimental results presented below.

11. The Role of Hydrogen Bubbles

In order to evaluate further the role of hydrogen bubble formation and release on AE measurements some experiments have been performed on 1018 steel in 42 v/o HCl and stainless steel type 304 in 3.5% NaCl. Figure 7 shows the typical increase of AE rates in the early stages of immersion which parallels the increase of corrosion rates monitored earlier for iron in 1N H_2SO_4 using polarization resistance measurements (5). Addition of an organic inhibitor (2-butyne-1,4-diol) decreased the rate of AE similar to the observed decrease of corrosion rates (6). Experiments in which the steel samples were polarized anodically or cathodically at a constant current in order to determine whether an increase of the corrosion rate or an increase of the H_2 evolution rate lead to increases of the rate of AE have been inconclusive until now due to problems with bubble evolution at the counter electrode, etc.

Results obtained with stainless steel type 304 in 3.5% NaCl are shown in Fig. 8 for the count rate and the total count under various experimental conditions. A large SS304 counter electrode was used in order to minimize gas evolution at and pitting of the counter electrode. Before electrolyte was introduced into the test cell the AE count rate was less than 6 counts/min., the count rate increased substantially when the electrolyte was added and then decreased with time. When a cathodic c.d. of 2 mA/cm^2 was applied, the rate of AE increased sharply followed by a slower increase during application of the cathodic current. When the current was interrupted, the AE rate dropped by more than two orders of magnitude. An anodic c.d. of 2 mA/cm^2 was then applied to initiate pitting. The AE rate increased again but showed large fluctuations which continued when the current was interrupted. The increase and the fluctuations of the AE rate during and after application of the anodic current could be the results of initiation and growth of pits on the SS304 surface.

CONCLUSIONS

The rate of acoustic emission seems to be qualitatively related to the corrosion rate. In the case of localized corrosion of Al alloys freely corroding or coupled to dissimilar metals AE rates reflect accurately the corrosion behavior of these alloys. Additional information becomes available concerning the statistical nature of the pitting process for Al alloys and stainless steel. Hydrogen evolution due to cathodic polarization increases the rate of AE significantly.

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Figure Captions

1. Experimental arrangement for recording of acoustic emission events.
2. Acoustic emission from Al 2024 in 3.5% NaCl. One hour uncoupled, 30 min. coupled, 30 min. uncoupled.
3. Count rate and potential of Al 2024 coupled to Zn and freely corroding in 3.5% NaCl.
4. Comparison of AE signals from Al 1100 and Al 2024 freely corroding or coupled to Cu.
5. Rate of AE as a function of time for Al 1100/Cu in 3.5% NaCl.
6. Typical AE bursts observed for Al 1100/Cu in 3.5% NaCl (see Fig. 5).
7. Rate of AE as a function of time for 1018 steel in 42 v/o HCl.
8. Rate of AE and accumulated counts for stainless steel type 304 in 3.5% NaCl at open circuit and at an applied cathodic or anodic current.

Table 1. Acoustic Emission from Al Alloys in 3.5% NaCl, $21 \pm 1^\circ\text{C}$.

	Uncoupled 60 min Counts/Min. r_o (mdd)		Coupled 30 min Counts/Min. r_A (mdd)		Uncoupled 30 min. Counts/Min.
Al 2024/Cu	41	5.25	497	68.4	85
Al 2024/Steel	50	5.25	130	43.4	117
Al 2024/Cd	32	5.25	0.5	11.2	97
Al 2024/Zn	42	5.25	50	24.6	385
Al 1100/Cu	1.5	0.24	5200	40.6	1.6
Al 1100/Steel	3.0	0.24	4550	30.4	1.3
Al 1100/Cd	1.1	0.24	1.0	1.5	0.9
Al 1100/Zn	5.0	0.24	3.3	8.8	12

Note: Corrosion rate data r_o , r_A are from Ref. 4.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

$20 \text{ KHz} < f(\text{JJB}) < 300 \text{ KHz}$
Al 1100/Cu 3.5% NaCl

Figure 6

Figure 7

Figure 8

ACOUSTIC EMISSION FROM CORRODING ELECTRODES

Viewgraphs Presented

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ACOUSTIC EMISSION FROM CORRODING ELECTRODES

MANSFELD AND STOCKER (J. ELECTROCHEM. SOC. 124, 1301 (1977))
HAVE GIVEN CORRELATIONS BETWEEN CORROSION RATES AND AE FOR
UNSTRESSED AL ALLOYS COUPLED TO DISSIMILAR METALS IN NaCl.

MANSFELD AND STOCKER (TO BE PRESENTED AT CORROSION/79) HAVE
EVALUATED AE FORM AL ALLOYS AND STAINLESS STEEL 304 UNDER
LOCALIZED CORROSION CONDITIONS.

CONCLUSION: AE TECHNIQUES SHOULD HAVE GREAT VALUE IN BASIC
CORROSION RESEARCH AND IN PRACTICAL MONITORING APPLICATIONS.
TRANSDUCERS CAN BE MOUNTED EXTERNALLY TO MONITOR (LOCALIZED)
CORROSION PHENOMENA.

FUTURE GOALS: DETERMINE SOURCES OF AE AND CORRELATE WITH
CORROSION MECHANISM(S).

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ACOUSTIC EMISSION FROM CORRODING ELECTRODES

PREVIOUS EFFORTS HAVE CONCENTRATED ON ACOUSTIC EMISSION (AE)
FROM STRESSED SAMPLES (SEE FOR EXAMPLE ASTM STP 505 AND 571)

RETTIG AND FELSEN (CORROSION 32, 121 (1976)) HAVE COMPARED
CORROSION RATES AND AE RATES FOR UNSTRESSED MATERIALS (STEEL
IN ACIDS AND AL ALLOYS IN NaCl)

DRJCHENKO ET AL (PROT. METALS 13, 236 (1977)) CONCLUDE:

"MICROACOUSTIC CORROSION PROCESSES SHOULD BECOME AN IMPORTANT
CORROSION DISCIPLINE."