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SULFUR-COOLED POWER REACTOR STUDY

Final Report

By
D. R. Sawle

December 1960

Aerojet-General Nucleonics
San Ramon, California

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By
Dr. D. R. Sawle

December 1960

Work performed under Contract No. AT(04-3)251
Project Agreement No. 4

Aerojet-General Nucleonics
A Subsidiary of Aerojet-General Corporation
San Ramon, California

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I. INTRODUCTION AND SUMMARY

The purpose of the Sulfur-Cooled Power Reactor Study has been to gather technical information on the corrosion and heat transfer characteristics of boiling sulfur in order to evaluate the feasibility of using a boiling sulfur cycle to extract energy from a nuclear reactor. This method of extracting energy from a reactor is being considered because of the significant increase in thermal efficiency which may be obtained at boiling temperatures around 1200°F.

Work on the program included a literature survey of past corrosion work, capsule corrosion tests, dynamic loop corrosion tests, and boiling heat transfer experiments.

A. FLUID CHARACTERISTICS

Sulfur is desirable for use in a binary vapor nuclear power plant because:

1. Its vapor pressure-temperature characteristics are suitable for a topping cycle over a steam power plant. (A boiling temperature of 1200°F corresponds to a sulfur vapor pressure of 150 psia.)
2. Use of the sulfur binary vapor cycle permits cycle efficiencies of about 50% for a top temperature of 1200°F. (Since it is difficult to superheat steam in a nuclear power plant, this is a considerable improvement over the simple steam cycle.)
3. The low neutron cross section of sulfur makes it suitable for use in a thermal reactor.

Sulfur has a number of unusual characteristics. It has a low electrical and a low thermal conductivity which hinders forced-convection heat transfer. However, boiling heat transfer is reasonably good. A polymerization reaction causes a discontinuity in the temperature-viscosity curve at 318°F, above which sulfur has a very high viscosity (peak viscosity 62 lb/ft sec). With higher temperatures, the viscosity returns to reasonable values.

B. CORROSION CHARACTERISTICS

For many years, sulfur has been handled at high temperatures by the chemical industry. In manufacturing CS_2 , stainless steels of the 300 series are used at $1600^{\circ}F$, but the corrosion rates are high (on the order of inches per year). In a reactor system, the corrosion rate of the containment material should be less than 5 mils/year at the desired operating conditions, and the fuel element cladding material should have a corrosion rate of even less (on the order of 2 mils per year).

Ceramic coatings of SiC on graphite are corrosion resistant to sulfur. Alloys containing aluminum are a general class of materials which appear to have considerable promise for resisting sulfur corrosion; for example zirconium with aluminum additions, titanium with aluminum addition, and various iron alloys with aluminum additions.

Another approach to the corrosion problem is to add phosphorous to the sulfur. Phosphorous forms a number of sulfides, all of which have boiling points in the desired range. The compound P_4S_3 is the most stable and appears to be considerably less corrosive, even though the form tested was not pure enough to obtain definitive results. Also, better thermodynamic characteristics (Appendix A) permit P_4S_3 to achieve essentially the same cycle efficiency at $1100^{\circ}F$ as is obtained at $1200^{\circ}F$ with sulfur. The combination of lowered temperature and lowered corrosion rates with P_4S_3 may allow the use of conventional stainless steels.

C. HEAT TRANSFER CHARACTERISTICS

The method of Addoms⁽¹⁾ or Cichelli and Bonilla⁽²⁾ can be used to predict the boiling burnout characteristics of sulfur. At atmospheric pressure ($832^{\circ}F$) this method indicates that about 300,000 Btu/ft² hr can be obtained and at $1200^{\circ}F$ 550,000 Btu/ft² hr is obtainable. In pool boiling experiments these values have been verified. Boiling sulfur experiments in a tube gave considerably lower values, but there is reason to believe that this may have been at least partially due to experimental difficulties (Section IV, Heat Transfer).

II. SUMMARY OF SULFUR CORROSION LITERATURE

Sulfur corrosion literature was surveyed with respect to materials, theory, metal composition, and fluid properties.

A. MATERIALS

1. Chromium Steels

Literature on ferritic and hardenable martensitic chromium steels was studied with respect to sulfur corrosion. In general, corrosion resistance to sulfur improves as the chromium content is increased, at least up to 25% Cr. ⁽³⁾

In sulfur vapor at 700°F, 12% and 17% Cr steels showed penetration less than 20 mils per year. ⁽⁴⁾ Below 900°F, resistance to H₂S increased to a maximum at 18% Cr and then held steady at higher proportions. ⁽³⁾ Above 900°F, Cr contents up to 28% continued to improve resistance to H₂S. ⁽³⁾ While the mode of attack by H₂S may differ from that of pure sulfur vapor, materials should be selected which are resistant to both.

The rates of attack by sulfur above 1000°F are too high for long term applications, except for high chromium alloys such as type 446 with 27% Cr. Because of brittleness, these alloys are not recommended for stressed service. At 1290°F, penetration was 102 mils per year for a 27.6% Cr, 0.12% C, 0.25% Ni steel. ⁽³⁾

2. Chromium-Nickel Steels

Below 1300°F, the addition of 8 to 20% Ni improves the corrosion resistance towards H₂S slightly. Above 1400°F, nickel appears detrimental. ⁽³⁾ In a zinc roasting furnace at 1650°F and again at 1920°F, nickel-free type 466 steel proved superior to nickel-bearing chromium steels. The atmosphere contained 5% SO₂. ⁽³⁾

In sulfur vapor at 700°F, penetration of type 316 was less than 2 mils per year. Type 304 was similar but exhibited occasional

pitting. Table I lists corrosion penetration for several stainless steels at 1300°F in flowing sulfur vapor.

TABLE I

CORROSION PENETRATION OF STAINLESS STEELS IN SULFUR VAPOR (FLOWING)⁶

Averages of two samples each, run 336 hours at 1300°F

<u>Designation</u>	<u>Type</u>	<u>Mils per Year</u>
302	18-8	252
304	18-8	222
310	25-20	199
316	20-12-Mo	216
321	18-10-Ti	193
330	18-35	252
333*	27-43	228
347	18-10-Cb-Ta	250

* One sample only.

3. Chromium-Aluminum Steels

Aluminum as an alloying metal improved corrosion resistance toward sulfur-bearing gases,⁽⁵⁾ but in high chromium steels 1.5% Al increased the weight gain in sulfur vapor over a 24-hour period.⁽⁶⁾ This may not be indicative of actual corrosion rates, however, as a 12% Cr - 4% Al steel (Carpenter 1JR) gave results superior to all steels in Table I, based on 350 hours in sulfur vapor.

4. Columbium Steels

Columbium as an additive to austenitic stainless steels imparts resistance to intergranular corrosion.⁽⁷⁾ Pure columbium, however, completely corroded to a white powder after 350 hours in sulfur vapor at 1300°F.⁽⁸⁾

5. Silicon Carbide

Silicon carbide refractories and SiC bonded with silicon nitride are not attacked by molten sulfur or sulfur vapor below 1250°F.

Atomic sulfur, which may be present in sulfur vapor as low as 1500°F, will attack silicon carbide to form silicon sulfides.⁽⁹⁾

6. Carbon

Carbon and graphite resist heat and some nonoxidizing atmospheres extremely well. A corrosion rate of less than 2 mils per year has been reported for carbon in contact with molten sulfur at 300°F, but at temperatures about 1400°F sulfur reacts rapidly with carbon powder to form CS₂.

B. THEORY

The corrosion of steel at elevated temperatures in molten sulfur has been described by Dravnicks who measured the electrical conductance of the remaining cross-section of thin strips of steel corroding in molten sulfur.⁽¹⁰⁾ The results were consistent with a rate of attack limited by diffusion through an adherent scale. This indicates that the corrosion rate goes as the square root of time rather than linearly.

Dravnicks observed cracking of the sulfide scale after prolonged corrosion, followed by a rapid increase in the local rate of corrosion until a new protective scale formed. He concluded that the two factors of diffusion through the scale thickness and spalling of the scale determine the rate of corrosion.

The layers of the sulfide scale, detected by microscopic and magnetic studies, were, in order: steel, non-magnetic pyrrhotite (FeS), magnetic pyrrhotite (FeS), and pyrite (FeS₂). The outer layer appeared to be pyrrhotite interpenetrated by pyrite. The inner layer of the scale was loose and powdery, and of a structure capable of rapidly conducting iron ions out to the pyrite-pyrrhotite interface.

Based on such a model, corrosion inhibition could be pursued by:

1. producing a more adherent scale,
2. reducing the reaction rate, and
3. slowing the diffusion rate by a denser scale or by interfering ions.

C. METAL COMPOSITION

Possibly because of its ability to raise the melting point of mixtures of sulfides,⁽³⁾ chromium is desirable for corrosion resistance of steel to sulfur. Nickel has the lowest-melting sulfide (1470°F as compared to 2820°F for CrS and 2180°F for FeS) of any of the structural metals and has been found to increase the rate of attack by sulfur-bearing vapors.

Resistance to oxidation is increased by adding silicon to chromium steels,⁽¹¹⁾ but the lower melting point of SiS₂ (1800°F), as compared to 3000°F for SiO₂, requires careful experimental checking of the value of silicon additions in a sulfur system.

The addition of Ce, Zr, Th, or Cs has helped to increase the oxidative life. The improvement may result from a lowered susceptibility of grain boundaries to attack because of the deoxidative power of the additive,⁽¹²⁾ or from the physical properties of the scale and the larger atomic volumes of the additives which impede diffusion.⁽³⁾ Cesium is also of interest because its sulfides actually contract with increasing cesium content and their density increases.⁽¹³⁾ A lattice defect with lanthanum, similar to that of Ce, suggests that La would demonstrate desirable properties as an additive against sulfur attack.

D. PROPERTIES

At proposed reactor temperatures, sulfur is in equilibrium between S₈, S₆, S₄, and S₂ molecules, but higher temperatures would make the highly reactive atomic sulfur state important and increase the corrosion problem many times.

Additions to the working fluid could aid the formation of an adherent scale. Since phosphorous tends to tie up the sulfur as phosphorous sulfides it could be expected to reduce the corrosion rate. The possible addition of one of the sulfur fluorides to provide a protective film against sulfur is analagous to the passivation of stainless steels by a nitric-hydrofluoric mixture.

III. CORROSION

Two main approaches were taken to the sulfur corrosion problem. One was to investigate alloys and alloy additions to the container, and the other was to investigate additives to the sulfur.

Aluminum and iron-aluminum alloys have been shown to have low corrosion rates in sulfur, and chromium also seems to improve corrosion resistance. Generally, it is desirable to have an adherent high melting point scale; therefore, it is expected that elements with high melting point sulfides will have good resistance.

One main approach in this program was to investigate alloys with high aluminum contents. Aluminum coatings were shown to be very helpful, but since a material with long term reliability is desirable no effort has been expended on coatings.

There are many additives which might be expected to modify the corrosion rate. Some of the compounds which were added are CS_2 , SO_2 and phosphorous. At 1200°F , sulfur is a mixture of S_8 , S_6 , S_4 and S_2 and the smaller molecules would be expected to produce higher corrosion rates. Additives which reduce the quantity of sulfur present as S or S_2 would be expected to reduce the corrosion rate. Phosphorous would be expected to have this effect since it forms various sulfur compounds. An additive might also promote formation of a protective scale.

A. SULFUR PURITY

Two types of sulfur were used in the tests: a high purity grade designated HP and the more common NF grade.

The high purity sulfur was specially prepared and obtained from General Chemical Corporation (99.9998% pure). Their analysis indicated a maximum of 2 ppm sodium. (AGN had a spectrographic analysis made and no metallic impurities were found, indicating agreement.)

The NF grade sulfur is the common National Formulary grade, (99.85% pure). A spectrographic analysis of this material indicated 200 ppm iron and no other metallic impurities.

There have been some indications that small concentrations of impurities and corrosion products from other types of materials may accelerate corrosion, so use of high purity sulfur is important to the results.

B. PRELIMINARY CAPSULE CORROSION TESTS

Preliminary refluxing tests were conducted in Vycor capsules, about 10 in. long and 1/2 in. ID. The capsules were filled with sulfur and additives and sealed under vacuum or under a controlled atmosphere. Stainless steel tubes, immersed in molten salt, held the capsules for the duration of the test. This permitted a large number of capsules to be heated in a uniform-temperature salt pot.

Sample preparation varied with the nature of the material as shown in Table II. Obvious surface coatings or irregularities were abraded and all samples were scrubbed with a slurry of Al_2O_3 and lightly pickled in nitric-hydrofluoric acid. Ford alloys were annealed at 1900°F .

After the test run, each sample was scraped to remove loose scale and washed with CS_2 to dissolve residual sulfur before weighing. After pickling in 10% HNO_3 to remove all scale, the samples were weighed again. Since dilute nitric acid attacks the Ford alloys, they were rinsed with HF in CS_2 to remove scale. Table III lists the results of the tests. Losses (in thickness) were calculated from weight loss after rough scale removal and after acid cleaning.

The most important factors in corrosion resistance are the density and adherence of the scale. If the scale maintains its integrity, the corrosion rate would diminish with the square root of time. Unless an alloy forms an adherent scale in static sulfur atmospheres, it cannot be expected to perform well under dynamic conditions.

Phosphorous appears to be the only additive with a significant effect on the corrosion rate, probably because phosphorous may be added in sufficient amount to eliminate free sulfur.

Corrosion rates are somewhat lower in high purity sulfur, containing less than 2 ppm impurities.

TABLE II

SAMPLE PREPARATIONPRELIMINARY CORROSION TESTS

<u>Alloy</u>	<u>Nominal Composition</u>	<u>Treatment</u>	<u>Pickle</u>
316	18 Cr 10 Ni 2.5 Mo	Rub with slurry Al_2O_3	Warm 50% HNO_3 , 5% HF, 5 min
Alleghany-Ludlum G-192	21 Cr 9 Mn 0.55 C Bal Fe	Rub with slurry Al_2O_3	5 min
C-120 AV	6 Al 4 V Bal Ti	One side abraded 1 mil with wet SiC cloth	5 min
Carpenter 1JR	13 Cr 4 Al	Rub with slurry Al_2O_3	5 min
Zr-Al	3 Al Bal Zr	Smoothed with wet SiC cloth	1 min
Zr	100 Zr	One side cleaned of oxide	1 min
Ford A	7 Al 4 Mo 0.6 Ti	Anneal 1900°F in air	1 min
Ford E	30 Mn 8 Al 1 Si 1.0 C	Anneal 1900°F in air	1 min

TABLE III

ALLOY - SS 316

1200°F

SPECIMEN NO.	ATMOSPHERE & SULFUR PURITY	OTHER ALLOYS IN SAME CAPSULE	TEST LENGTH (HOURS)	THICKNESS	WEIGHT BEFORE	SCALE LOSS mils	TOTAL LOSS AFTER ACID CLEANED		
							mils	grams	mils/yr
B7	vac, NF	1JR, G192	300	.076	11.4053	2.0	2.4	.7270	71
B8	air vac, NF	1JR, G192	300	.069	11.8501	.5	.7	.2369	20
B9	vac, NF	1JR, G192	150	.065	11.4260	.2	.8	.2794	46
12	SO ₂ NF	1JR, G192	150	.064	12.5536	.8	1.0	.3776	56
13	SO ₂ NF	1JR, G192	300	.063	12.6134	1.3	1.4	.5814	42
14	vac, HPS	1JR, G192	150	.064	12.7180	.5	.8	.3096	45
11	vac, HPS	1JR, G192	300	.063	12.5781	.9	1.3	.5233	38
B4	NF CS ₂	1JR, G192	150	.063	11.8718	.8	1.1	.4258	66
B15	NF CS ₂	1JR, G192	300	.063	12.4498	1.6	1.7	.6747	50
B16	NF P ₂ S ₅	1JR, G192	150	.063	12.2930	.2	.2	.0810	12
B17	vac, P ₂ S ₅	1JR, G192	300	.063	12.2904	.3	.4	.1459	11
B19	vac, P ₂ S ₅	-----	150	.063	15.7737	.9	1.2	.5997	70

TABLE III (cont'd)

ALLOY - 1JR

1200°F

SPECIMEN NO.	ATMOSPHERE & SULFUR PURITY	OTHER ALLOYS IN SAME CAPSULE	TEST LENGTH (HOURS)	THICKNESS	WEIGHT BEFORE	SCALE LOSS mils	TOTAL LOSS AFTER ACID CLEANED		
							mils	grams	mils/yr
A8	vac, NF	SS 316, G192	300	.040	6.9795	2.6	3.4	1.1970	100
A9	air vac, NF	SS 316, G192	300	.041	7.2464	1.6	2.1	.7408	61
A10	vac, NF	SS 316, G192	150	.047	7.0180	.4	1.3	.3795	74
A12	SO ₂ NF	SS 316, G192	150	.040	6.5758	.5	1.2	.4005	71
A13	SO ₂ NF	SS 316, G192	300	.041	7.2748	1.4	2.2	.7755	64
A14	vac, HPS	SS 316, G192	150	.040	7.2803	.2	.6	.3561	37
A15	vac, HPS	SS 316, G192	300	.040	7.0286	.4	.5	.2570	30
A5	NF CS ₂	SS 316, G192	150	.040	6.9795	1.6	2.1	.7388	124
A16	NF CS ₂	SS 316, G192	300	.036	6.2393	1.1	1.7	.5908	50
A17	P ₂ S ₅	SS 316, G192	150	.036	5.9640	.0	.6	.2113	37
A18	P ₂ S ₅	SS 316, G192	300	.036	6.5467	.2	.4	.2572	21

TABLE III (cont'd)

ALLOY - G192

1200°F

SPECIMEN NO.	ATMOSPHERE & SULFUR PURITY	OTHER ALLOYS IN SAME CAPSULE	TEST LENGTH (HOURS)	THICKNESS	WEIGHT BEFORE	SCALE LOSS mils	TOTAL LOSS AFTER ACID CLEANED		
							mils	grams	mils/yr
C5	vac, NF	SS 316, 1JR	300	.036	9.8112	1.2	1.6	.8888	48
C6	air vac, NF	SS 316, 1JR	150	.055	6.1890	.8	1.7	.3801	99
C7	vac, NF	SS 316, 1JR	150	.050	6.2654	1.0	2.3	.5786	135
C12	SO ₂ , NF	SS 316, 1JR	150	.035	6.9759	.7	1.2	.4827	71
C13	SO ₂ , NF	SS 316, 1JR	300	.034	7.1610	1.1	1.6	.6954	48
C11	vac, HPS	SS 316, 1JR	150	.035	6.7723	1.1	1.5	.4116	62
C9	vac, HPS	SS 316, 1JR	300	.036	7.0983	.8	1.8	.6737	50
C2	NFS, CS ₂	SS 316, 1JR	150	.036	4.6915	.1	1.6	.4055	91
C15	NFS, CS ₂	SS 316, 1JR	300	.034	6.8281	1.1	1.7	.6726	49
C16	vac, P ₂ S ₅	SS 316, 1JR	150	.035	6.9614	.2	.8	.3336	49
C17	vac, P ₂ S ₅	SS 316, 1JR	300	.035	6.4850	.3	1.0	.3535	28

TABLE III (cont'd)

CORROSION DATA

SPECIMEN NO.	ATMOSPHERE & SULFUR PURITY	TEMP °F	OTHER ALLOYS IN CAPSULE	TEST LENGTH (HOURS)	THICKNESS	WEIGHT BEFORE	SCALE LOSS mils	TOTAL LOSS AFTER ACID CLEANED		
								mils	grams	mils/yr
SS 316	HPS, vac	1120	-----	600	.064	14.4032	----	.8	.3520	11.4
SS 316 HT	HPS, vac	1120	-----	600	.063	15.0467	.5	.8	.2928	11.7
SS 202 2B	HPS, vac	1120	-----	600	.048	7.9793	1.0	1.1	.3604	15.8
SS 202 HT	HPS, vac	1120	-----	600	.049	7.4972	.4	.6	.1893	9.1
TiAl E1	NF	1200	ZrAl	150	.092	5.5464	.5	.5	.0578	28
TiAl E2	NF	1200	ZrAl	300	.091	5.1103	.8	.8	.0899	23
TiAl	HPS, vac	1120	-----	600	.089	5.3038	.5	.5	.0636	7.7
TiAl HT	HPS, vac	1120	-----	600	.094	5.6483	----	--	+.0016	----
FORD E F1	NF, vac	1200	FORD A	300	.052	7.0850	----	--	.2817	30 (1)
FORD E	NF, vac	1120	-----	600	.050	2.2940	----	--	+.0080	----
FORD E HT	NF, vac	1120	-----	600	.048	2.0681	----	--	.0126	2.0
FORD E HT	NF, vac	1120	-----	300	.051	2.3171	----	--	.0030	.91
FORD E HT	NF, vac	1120	-----	300	.056	2.5910	----	.2	.0239	7.30
FORD E HT	NF, vac	1120	-----	600	.382 (2)	12.7801	+.1525g (3)	--	-----	-----
FORD E HT	NF, vac	1120	-----	600	.376 (2)	-----	----	--	.0146	2.80
FORD A J1	NF, vac	1200	FORD E	300	.055	8.8608	----	3.0	.9820	89
ZrAl H1	NF	1200	TiAl	150	.109	9.5557	.2	.2	.0356	12
ZrAl H2	NF	1200	TiAl	300	.107	11.4327	.7	.7	.1513	21
ZrAl	HP, vac	1120	-----	600	.105	12.2292	1.8	3.4	.7790	49
ZrAl HT	HP, vac	1120	-----	600	.107	10.5273	----	--	+.0405	----

(1) Some metal removed as well as scale

(2) Diameter

(3) Large growth on one corner

The samples of Carpenter 1JR showed poor corrosion resistance and a relatively loose scale. While 1JR resists sulfur vapor, it is attacked by the liquid phase so that the Stauffer tests, ⁽⁶⁾⁽⁸⁾ conducted in the vapor phase, indicated a good resistance which is misleading for our purposes. In general, alloys containing 5 to 10% aluminum show better corrosion resistance. This was indicated previously by the Stauffer data and also by the fact that impervious aluminum coatings have worked well.

Ford Alloy "E" (28-30 Mn, 7.5-8.5 Al, 0.9-1.1 Si, 1.C, Bal Fe) shows good corrosion resistance with a very adherent scale in the preliminary tests. With its high-temperature strength it is the most promising type of alloy for sulfur service. Heating of this alloy to 1350°F in air decreased the resistance to sulfur, probably because of formation of manganese dioxide scale. (C-120 AV and Zr-3Al showed improved corrosion resistance after the same treatment, due to the protective nature of the oxides.)

C. LONGER TERM CORROSION TESTS

1. Stainless Steel

Type 316 stainless, as shown in Table IV, has moderate resistance to sulfur attack. However, there is a large difference between the results from the first six samples run in a large salt pot and those from the last four which were run in a small crucible furnace, due to failure of the large vessel. The conditions differed in two respects: temperature oscillations and refluxing. Temperature varied considerably more in the small vessel; the control was set to maintain temperature of at least 1200°F but there were oscillations to 1230°F. Because of the small size of the vessel, only the lower ends of the Vycor capsules could be maintained at temperature, so that the refluxing rate was considerably higher than with the first six samples in the large vessel.

Sample numbers B42 and B45 were in the large salt pot at the time of its corrosion failure and could not be removed without

TABLE IV
TYPE 316 STAINLESS TESTS

TEST NO.	TEMP °F	ATMOSPHERE	PURITY	DURATION (hrs)	THICK (in)	LOSS	
						(mils)	(mils/yr)
B24	1200	vac	HP	600	.061	.6	9
B28*	1200	vac	HP	600	.062	.7	10
B34	1200	vac	HP	600	.063	.6	9
B35*	1200	vac	HP	600	.064	.6	9
B36	1200	vac	HP	600	.068	.8	11
B37*	1200	vac	HP	600	.065	.6	9
B42	1200	vac	HP	400	.063	6.2	136
B45*	1200	vac	HP	400	.063	8.0	176
B50	>1200	vac	HP	505	.062	1.8	32
B51*	>1200	vac	HP	505	.062	1.7	30
B52	>1200	vac	HP	624	.063	2.1	30
B53*	>1200	vac	HP	624	.063	1.9	27

* Heated in air at 1300°F for ½ hour.

breaking their capsules. It is probable that the capsules were cracked before removal and that the high recorded corrosion rates were due to traces of chloride from the salt bath.

Samples preheated at 1300°F in air showed no significant difference in corrosion resistance. Therefore, oxide coatings do not appear to be a factor in the resistance of 316 stainless steel to sulfur attack.

A sample of 316 stainless steel was suspended in the high velocity leg of the dynamic loop. It had completely disintegrated at the end of the 447 hour test, which was run at 1200°F with NF grade sulfur.

A photomicrograph of a stainless steel sample after exposure to sulfur is shown as Figure 1. There is no evidence of intergranular attack.

2. Graphite

The results of corrosion tests on bare and coated graphite are given in Table V. The erratic weight changes of the bare graphite samples indicate that sulfur can both penetrate and erode graphite at this temperature. The results indicate that further study is necessary but it is probable that graphite to be used in a sulfur atmosphere will require a suitable protective coating. High density graphite was more resistant while the porous, lower density type (first specimen) was more corroded.

The silicon carbide coating on six of the graphite samples provided an effective protection against sulfur corrosion. Surface defects allowed some corrosion in two of the samples.

3. Zirconium-3% Aluminum

Zirconium with 3% aluminum has reasonably good resistance to sulfur attack and because of its very low neutron cross-section, would be an excellent material for use within a reactor. Results of corrosion

FIGURE 1

316 STAINLESS STEEL

FIGURE 2

Zr-Al ALLOY
-17-

TABLE V
GRAPHITE CORROSION TESTS

MATERIAL	TEMP °F	ATMOS	PURITY	DURATION (hrs)	DIAMETER (in)	SURFACE LOSS	
						(mils)	(mils/yr)
Bare Graphite	1120	vac	HP	600	.250	4.2	61
Bare Graphite	1200	vac	HP	600	.250	0	<.1
Bare Graphite	1200	vac	HP	280	.250	slight weight gain	
Bare Graphite	1200	vac	HP	280	.250	slight weight gain	
SiC coating	1120	vac	HP	600	.253	0	<.1
SiC coating	1120	vac	HP	600	.253	.4	6
SiC coating	1200	vac	HP	600	.252	0	<.1
SiC coating	1200	vac	HP	600	.253	0	<.1
SiC coating*	1200	vac	HP	280	.252	.4	13
SiC coating*	1200	vac	HP	280	.252	.5	16

* Had surface defects

tests are given in Table VI. The properties of this alloy are discussed in Appendix B. The data indicates that there may be some value in a thin protective preoxidized surface. Mechanical grinding is apparently detrimental.

The results were not as consistent as has been hoped. This may have been due to differences in the refluxing rate in the capsules and to slight variations in the temperature of the capsules. The addition of H_2O appears to make a small increase in the corrosion rate. The presence of SO_2 does not seem to modify the corrosion rate appreciably.

A photomicrograph of the Zr-3% Al alloy after removal is shown in Figure 2. No evidence of penetration or corrosion below the surface is evident.

A dynamic test was made with a sample suspended in the high velocity boiling leg of the loop. A description of the dynamic loop is given in Section IV (Heat Transfer). It is a natural convection boiling loop. For the corrosion tests the heat transfer test section was replaced with a section of 1 in. pipe with "calrod" heaters and a holder for a number of corrosion test samples. A test of 447 hours duration was made at $1200^{\circ}F$. The velocity varied during the run between 1 and 5 ft/sec. For this test, four samples were used: zirconium aluminum, titanium aluminum, Ford Alloy "E" and 316 stainless steel.

This test indicated a corrosion rate on the zirconium aluminum of approximately double the static tests (108 mils/year linearly extrapolated corrosion rate). The samples after removal are shown in Figure 3. (The longer sample is the Zr-Al.)

The scale and the sulfur from sample H-14 was analyzed spectrographically with the results shown in Table VII. The impurities were from the ZrAl.

4. Titanium Aluminum (C 120 Av)

The titanium aluminum alloys are a possible class of alloys of interest for structural materials. Results of corrosion tests

TABLE VI

ZIRCONIUM-ALUMINUM TESTS

TEST NO.	TEMP OF	ATMOS	PURITY	DURATION (hrs)	THICKNESS (in)	WEIGHT LOSS (mils) (mils/yr)	
H5 ¹	1200	vac	HP	600	.105	5.0	73
H6 ¹	1200	vac	HP	600	.107	slight weight gain	
H9 ¹	1200	vac	NF	400	.107	2.9	63
H10 ²	1200	vac	NF	400	.108	3.1	67
H12 ¹	1200	vac	HP	505	.092	2.1	37
H13 ²	1200	vac	HP	505	.092	.1	3
H14 ¹	1200	vac	HP	624	.092	2.9	41
H15 ²	1200	vac	HP	624	.093	2.4	34
H20 ^{2,3}	>1200	H ₂ O	HP	280	.088	2.0	62
H21 ³	>1200	H ₂ O	HP	280	.093	2.3	72
H23 ^{2,3}	>1200	SO ₂	HP	280	.095	.4	11
H24 ³	>1200	SO ₂	HP	280	.092	2.1	65
H17 ³ (dynamic test)	1200	vac	NF	447	.115	5.5	108

1. Hand rubbed
2. Oxidized at 1300°F in air for 30 minutes
3. Surface ground by machine (abrasive was SiC) but not annealed.

FIGURE 3

SAMPLES AFTER DYNAMIC CORROSION TEST

TABLE VII

SPECTROGRAPHIC ANALYSIS OF ZrAl SCALE + SULFUR

	<u>Scale</u>	<u>Sulfur</u>
Mg	0.001	0.005
Al	1.5	0
Si	0.005	0
Cr	0.006	0
Mn	0.006	0
Fe	0.15	0
Ni	0	0
Cu	0	0
B	0	0
P	0	0
Ca	0	0
Ti	0	0
Zr	60	0.08
Ba	0	0

Note: The above are reported as the oxides of elements indicated.

are shown in Table VIII. The neutron absorption cross section is rather high for use in the reactor core. The high-temperature strength is not as good as might be desired, but newer alloys are being developed with improved high-temperature strength.

An oxide coat on the metal seems to improve the corrosion resistance of titanium aluminum just as it does on zirconium. NF grade sulfur appears to give higher corrosion rates than does high purity sulfur. The dynamic test of the titanium aluminum alloy gave appreciably higher corrosion rate - approximately double the static rate. The flow rate varied from 1-5 ft/sec.

A photomicrograph of the titanium aluminum alloy after removal from the sulfur is shown as Figure 4. There was no evidence of intergranular attack.

5. Iron Manganese Aluminum Alloys (Ford "E")

In the preliminary tests, one of the alloys showing most promise was an iron manganese aluminum experimental austenitic alloy (composition: 28-30 Mn, 7.5-9.10 Al, 0.9-1.1 Si, 1C Bal Fe) developed by Ford Motor Company and designated Ford Alloy "E". It has excellent high temperature strength and is relatively easy to fabricate and weld. (See Appendix A for further discussion.) Because of its high aluminum content and the absence of nickel, it was expected to have good sulfur corrosion resistance. The early tests indicated this was true.

A second batch (Heat Z-336 A, analysis in Table IX) of this material was obtained with slightly higher aluminum as this was expected to reduce corrosion. However, this led to some problems in metallurgical instability. Corrosion testing of samples in the cold work condition (without anneal) at 1200°F caused a precipitation of transformation, and the alloy became ferritic. Table X shows the results of corrosion testing. All the samples were from Heat Z-336 A except for the sample F1 which was a sample from the first batch and had previously

TABLE VIII
TITANIUM-ALUMINUM (C 120 AV) TESTS

SAMPLE NO.	TEMP °F	ATMOS	PURITY	DURATION (hrs)	THICKNESS (mils)	WEIGHT (gm)	WEIGHT LOSS		
							(gms)	(mils)	(mils/yr)
E10	1120	vac	HP	600	.088	5.3038	0.0636	0.53	7.7
E11	1120	vac	HP	600	.092	5.6483	+.0026	----	---
E12	1200	vac	HP	400	94	5.5478	0.7210	6.	130
E13*	1200	vac	HP	400	89	5.1217	0.1900	1.6	35
E17 Dynamic	1200	vac	NF	447	89	5.1219	1.5692	13.6	300

* Heated at 1300°F for ½ hour in air.

FIGURE 4

Ti-Al ALLOY

FIGURE 5

Fe Mn Al ALLOY

Nital Etch

Magnification 250x

240 hours exposure sulfur at 1200°F

Sample F-71

TABLE IX

ORIGINAL ANALYSIS OF HEAT Z-336 A (UNSTABLE)

<u>Manganese</u>	<u>Aluminum</u>	<u>Silicon</u>	<u>Carbon</u>	<u>Iron</u>
29.50	9.91	1.03	1.00	Balance

ORIGINAL ANALYSIS OF ALLOY "E" - (STABLE)

<u>Manganese</u>	<u>Aluminum</u>	<u>Silicon</u>	<u>Carbon</u>	<u>Iron</u>
30.35	7.85	1.02	1.00	Balance

TABLE X

IRON MANGANESE ALUMINUM ALLOY TESTS

(FORD "E")

SAMPLE NO.	ALLOY	TEMP °F	ATMOS	PURITY	DURATION (hrs)	THICK (in)	WEIGHT BEFORE (gms)	WEIGHT LOSS		
								(gm)	(mils)	(mils/yr)
F67	Z-336A	1200	vac	HP	624	0.051	5.8512	1.4326	6.2	62
F68*	Z-336A	1200	vac	HP	624	0.046	5.1578	badly broken		
F69	Z-336A	1200	vac	HP	624	0.045	4.9806	dissolved		
F70*	Z-336A	1200	vac	HP	624	0.050	5.7796	dissolved		
F71	Z-336A	1200	vac	HP	240	0.046	4.8162	0.2792	1.3	48
F72	Z-336A	1200	vac	HP	240	0.049	5.6630	0.2189	0.95	35
F1	"E"	1200	vac	HP	280	0.047	4.5749	1.8515	9.5	300
F90	Z-336A		vac	HP	280	0.046	7.6984	3.2523	9.7	300
F91*	Z-336A		vac	HP	280			dissolved		
F92	Z-336A		SO ₂	HP	280	0.046	7.8476	4.0071	12.0	375
F93*	Z-336A		SO ₂	HP	280	0.046	7.5745	4.5245	13.7	428

* Heated for ½ hour at 1300°F in air.

been tested in sulfur with reasonably good results. In this particular test it has a corrosion rate similar to the samples from the second batch. Sample F1 did maintain reasonable ductility and remained austenitic while the remainder of the samples were transformed to ferrite and carbides and were very brittle.

In general, all the recent tests of the higher aluminum alloy gave rather erratic results. The following possible explanations for this behavior are being investigated.

a) The previous tests gave low corrosion rates which are representative of the single phase austenitic alloy.

b) The fact that F90 and F91 were in the same capsule and corroding at a very rapid rate may have influenced the corrosion rate of sample F1.

c) Heat Z-336-A samples after removal from the sulfur appeared to have undergone a transformation. After removal from the capsules, the samples were magnetic. This, and observation of the photomicrograph (Figure 5), indicates a transformation to ferrite and possible carbides. This is probably due to the cold worked condition plus the instability due to the large percentage of aluminum in the alloy. (Figure 6 shows a photomicrograph of a sample of the stable Alloy "E" after removal from the sulfur.)

d) The corrosion rate may be a very steep function of temperature. The results which were good were from tests at a temperature of 1120°F. The sample which was at 1200°F in the preliminary tests has a higher corrosion rate which, extrapolated linearly, was 30 mils/yr. The true corrosion rate is probably more nearly parabolic with time.

e) There may have been impurities in the later tests which could have accelerated the corrosion rate. The corrosion products from one of the samples which completely disintegrated were analyzed and the results of this analysis are contained in Table XI. The analysis for sulfur and chlorine indicates that there was some chlorine present

Fe-Mn-Al ALLOY

FIGURE 6

TABLE XI

SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS

The following are reported as the oxides of the elements indicated

Magnesium (Mg)	0.0005%	Manganese (Mn)	25.%
Aluminum (Al)	5.%	Iron (Fe)	40.%
Silicon (Si)	1.%	Nickel (Ni)	.015%
Calcium (Ca)	.1%	Copper (Cu)	.0005%
Chromium (Cr)	.015%	Barium (Ba)	.04%

QUANTITATIVE ANALYSIS FOR SULFUR AND CHLORINE

Total Sulfur (S)	54.1%	Total Chlorine (Cl)	.11%
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which probably produced a very corrosive effect. Calcium and barium could have a bad effect since they tend to produce atomic sulfur. This particular sample contained HP sulfur and was one of the longer term tests in which there might have been a cracked capsule; if this were the case, the capsule would have leaked since the salt had seriously corroded the stainless capsule holder.

The scale from samples F67 and F69 was analyzed spectrographically and the results are shown in Table XII. The results show the expected steel scale composition characteristics.

A specimen of the second batch of Ford Alloy "E" (Heat Z-336 A) was suspended in the hot leg of the sulfur loop. The test was for 447 hours at 1200°F with NF grade sulfur and the sample completely disintegrated.

D. PHOSPHOROUS AS AN ADDITIVE

Phosphorous forms a number of sulfur compounds (P_2S_5 , P_4S_7 and P_4S_3), all of which have vapor pressure characteristics very similar to sulfur. P_4S_3 is the most interesting since it is the most stable (molecular weight is constant to 1300°F) and it does not exhibit the increased viscosity as does sulfur and P_2S_5 and P_4S_7 . Its properties are discussed further in Appendix A.

Results of corrosion tests are shown in Table XIII. Short term tests indicate that it has relatively low corrosion rates on 316 stainless steel at 1200°F. Since it has better thermodynamic characteristics, it could be operated at a considerably lower temperature to obtain the same power plant efficiency.

The P_4S_3 as used in these tests was a commercial grade available from Hooker Electrochemical Company. It contains a considerable number of impurities, as shown in the spectrographic analysis of Table XIV. Further purification should reduce the corrosion rates.

TABLE XII

SCALE

	<u>Sample F67</u>	<u>Sample F69</u>
Mg	--	0.001
Al	4.5	6
Si	1.25	0.5
Cr	<.001	0.001
Mn	15	20
Fe	20	30
Ni	0.015	0.02
Cu	--	--
B	--	--
P	--	--
Ca	--	--
Ti	--	--
Zr	--	--
Ba	--	--

Note: All numbers are reported as oxides of the element.

TABLE XIII
PHOSPHOROUS ADDITIVES

SPECIMEN TYPE & NO.	ATMOSPHERE	TEMP °F	TEST LENGTH (hrs)	THICKNESS	WEIGHT BEFORE	CORROSION LOSS		
						(gms)	(mils)	(mils/yr)
SS 316 B 58 HT*	P ₄ S ₃	1200	120	.062	12.7558	.0928	0.2	17
SS 316 B59	P ₄ S ₃	1200	120	.061	16.5710	.0538	0.1	7.2
FORD E F 82 HT*	P ₄ S ₃	1200	120	.056	6.6801	.0378	0.16	12
FORD E F 83	P ₄ S ₃	1200	120	.056	7.1032	.0501	0.2	14
FORD E F 44	P ₄ S ₃	1200	200	.110	11.5902	.0165	.08	3.4
FORD E F 45	P ₄ S ₃	1200	200	.112	13.6956	.0197	.08	3.4
FORD E F 46	P ₄ S ₃	1200	200	.110	12.4823	.0058	.03	1.1
FORD E F 47	P ₄ S ₃	1200	200	.111	11.5095	.0001	---	.1
SS 316 B27	P ₂ S ₅	1200	600	.063	12.5038	.5832	1.5	22

* HT indicates heat treated at 1300°F in air for ½ hour.

TABLE XIV

SPECTROGRAPHIC ANALYSIS OF P_4S_3

Mg 0.12	Cu 0.04
Al 0.15	B --
Si 2.5	P 15
Cr --	Ca 0.12
Mn 0.004	Ti 0.02
Fe 0.35	Zr --
Ni --	Ba 0.002

Note: All numbers are reported as oxides of the elements.

IV. HEAT TRANSFER TO BOILING SULFUR

A. ANALYTICAL TREATMENT

The boiling burnout heat flux may be calculated by the method of Addoms⁽¹⁾ where:

$$(q/A)_p = 2 \rho_v \lambda \left[\frac{\rho_L - \rho_v}{r} \right]^{0.63} \left[g \left(\frac{k}{\rho c_p} \right)_L \right]^{1/3}$$

where:

$$\begin{aligned} (q/A)_p &= \text{peak heat flux} \\ \rho_v &= \text{density of vapor} \\ \rho_L &= \text{density of liquid} \\ \lambda &= \text{heat of vaporization} \\ g &= \text{acceleration of gravity} \\ k &= \text{conductivity} \\ c_p &= \text{heat capacity} \end{aligned}$$

This expression gives a boiling burnout heat flux of 550,000 Btu/hr/ft² for sulfur at 150 psi. This was checked with the method of Cichelli and Bonilla and found to be essentially identical. The critical temperature difference was found to be 45°F.

B. POOL BOILING

For comparison with heat transfer in the sulfur loop, a test of pool boiling at atmospheric pressure was made using a horizontal wire. A heating element of 20-mil chromel wire, 7/8 in. in length, reached boiling burnout at a heat flux of 424,000 Btu/hr/ft². Calculations using the method of Cichelli and Bonilla indicated a burnout flux of about 300,000 at atmospheric pressure.

Several tests were made using a horizontal strip 0.125 in. wide and approximately 1 in. in length. The first test gave a burnout flux of 311,000 Btu/hr ft² and the second test a burnout flux of 275,000.

C. DYNAMIC LOOP MEASUREMENTS

For measurement of boiling heat transfer a natural convection loop was constructed to operate with boiling sulfur. It was felt that the pump presented special problems considering the viscosity of the sulfur and the high temperature, and that some data could be obtained with a natural convection loop. A pump could be added to the system later.

Figure 7 shows the direction of flow in a schematic drawing of the loop. Figure 8 shows the downcomer on the right, leading into the flowmeter and preheater sections, and then up into the narrow test section with its surrounding copper block, also shown in Figure 11. The heat pump is above the test section. This photograph was taken before the thermocouples and insulation were installed. The heat pump provides a method of increasing the flow rate by increasing the amount of vapor, thus decreasing the density of the hot leg.

The test section consists of a high-purity copper block shrunk into a 1/4 in. ID 316 stainless tube. The second series of tests used a liquid metal between copper and stainless steel. The surface of the copper cylinder carries a helical groove and is coated with an insulating ceramic. A nichrome ribbon wound in the groove is electrically heated. The large heat capacity of the block slows the temperature rise at burnout.

Direct electrical heating of the test section could be used in the present loop. However, this approach requires good instrumentation since the heat capacity of the test section is very small; thus, the uncooled rate of temperature rise is very rapid at burnout. This, plus the relatively high corrosion rate of sulfur on stainless steel, increases the probability of the release of sulfur at burnout. Release of sulfur at these conditions would cause considerable damage to the loop.

Figure 10 shows the upper part of the loop. Rising wet sulfur vapor enters the separator chamber on the left, and returning liquid crosses to the downcomer in a pipe hidden by the beam. Vapor rises past the cold leg and condenses in the slanting harp. Note that the cold leg in the

SULFUR LOOP SCHEMATIC

FIGURE 7.

FIGURE 8

DYNAMIC SULFUR LOOP. LOWER SECTION

TEST SECTION

FIGURE 9

DYNAMIC SULFUR LOOP. UPPER SECTION

FIGURE 10

DYNAMIC SULFUR LOOP ENCLOSURE

FIGURE 11.

schematic drawing (Figure 7) is shown extended in the opposite direction for convenience. The condenser was found to be more effective than expected; it was necessary to add a heater and insulation to the condenser.

Figure 11 shows the loop in its housing with the upper access doors open.

The method of measuring the burnout flux consisted of the following:

1. The system was evacuated with a vacuum pump.
2. The entire loop was heated to 500°F by using approximately 20% of power on all heaters. Thermocouples were then checked at about 15 minute intervals to modify the heater settings as required. It generally required about three hours to reach temperature, due primarily to the low conductivity of stainless steel. If too high a heating rate was used during warmup, insufficient time was available for the heat to diffuse.
3. The system was evacuated a second time to remove trapped air.
4. Warmup was continued.
5. Temperature controls were set on the separator pot. The controller on the separator pot acted as the pressure controller for the system controlling the saturation temperature and pressure. This operated very satisfactorily and gave excellent control.
6. The flow rate was adjusted by modifying the heater setting on the heat pump.
7. The flow rate was measured by temperature rise across the heater of known power input.
8. The test section power was increased in approximately 10% increments. This was done until the test section temperature did not stabilize at a given temperature but continued to rise. This was the

power required at the apparent burnout flux. The heat losses were found by the temperature drop in the insulation surrounding the test section. The apparent burnout flux was calculated from the power input minus the heat losses, divided by the heat transfer area of the test section.

The parameters for a number of experimental runs are shown in Table XV. The earlier runs (series B and C) show a high film drop and relatively low apparent burnout flux. The test section carried a scale deposit on the inside surface which acted as an insulator. The non-uniformity of the insulating layer caused a high peak-to-average flux and gave a low apparent burnout flux.

The test section was rebuilt using a platinum clad tube to remove the effect of scale deposit on the inside of the test section. A corrosion test run of 447 hours was made after the first heat transfer runs. It was necessary to take the loop apart after this run and clean it, since the loose scale had built up in the loop by the end of the run so that there was very little flow. However, even after cleaning it was not possible to attain flow rates similar to those which had been obtained earlier. The low flow rate gives a high exit quality with a rather low apparent burnout point. The loop will be re-examined for evidence of loose scale which could reduce the flow rate in the test section. In the next phase of the program, it is planned that a pump will be added to obtain higher flow rates.

It is recommended that the data shown be regarded as preliminary, and subject to modification when further experimental results are available. The values of apparent burnout flux are the values obtained from the power input to the test section minus losses divided by the heat transfer area.

The following reasons are being investigated for the low burnout flux and high film drop:

TABLE XV

PRELIMINARY HEAT TRANSFER DATA

TEST NO.	T _{sat} (°F)	PRESSURE (psig)	FLUX ₂ (Btu/hr ft ² °F)	SUBCOOLING (°F)	FILM DROP (°F)	FLOW RATE (lb/hr)	EXIT QUALITY %	APPARENT BURNOUT FLUX
B-5	900	12	43,000	14	171	135	1	51,000
B-11	1140	84	145,000	42	233	350	2	no burnout
C-1	1000	35	94,640	46	205	52	10.8	no burnout
C-2	1000	35	115,440	44	395	51	16.3	133,000
C-4	1205	142	93,444	75	222	85	no net boiling	
C-5	1200	136	107,578	56	288	98	1	burned out nichrome ribbon @ 20% higher power
D-1	1100	72	116,000	85	279	17	32.6	Burnout @ 10% higher flux

1. Low flow rate with a high vapor quality at the exit caused by a restricted flow.
2. Possibility of a temperature drop between the stainless steel-copper innerface. In the last test (D-1) this innerface was filled with liquid metal, thus making this possibility very unlikely.

V. SULFUR HANDLING PROBLEMS

Handling sulfur at 1200°F and 150 psi presents a number of unique problems. Some of the approaches which have been used in this program are discussed below.

The dynamic loop was built using ring-joint flanges. This approach to static seals worked very well and there was essentially no difficulty encountered with leaks. Pressure measurement was made using a conventional Bourdon tube gage filled with a hydraulic oil and separated from the sulfur by a diaphragm. Since the hydraulic oil does not withstand the high temperature, it is necessary to use a cold leg for the purpose of measuring pressure. This is done by connecting a liquid leg to the vapor part of the loop and controlling its temperature to the desired value. The rupture disk assembly is also attached to the cold leg.

The rupture disk posed a problem. At the beginning, a monel rupture disk was used; although it was maintained below 500°F, corrosion reduced its strength sufficiently so that it released the sulfur to the atmosphere. The loop was operating at a temperature of 1200°F and 150 psia. The temperature and pressure melted a hole in the aluminum roof of the enclosure. The disk was replaced with a gold-plated diaphragm which had been properly baked to remove any hydrogen embrittlement and it operated satisfactorily. A platinum rupture disk could also have been used.

At 1200°F the sulfur forms a loose scale on the stainless steel. After prolonged operation it is necessary to clean the loop. If a large enough trap had been provided in the lowest part of the loop, the need for cleaning a large part of the loop might have been avoided.

Measurements of the sulfur stream temperature were made with Conax fittings. This type fitting extends the thermocouple into the stream. It was found desirable to gold plate these fittings to prevent scale buildup on the surface.

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APPENDIX A

PROPERTIES OF PHOSPHOROUS SULFIDE

I. GENERAL PROPERTIES

Since phosphorous appeared to have some value as an additive in amounts sufficient to form phosphorous sulfides, the properties of the most promising sulfide, P_4S_3 , are of interest. Phosphorous "sesquisulfide" is the most stable of the three established sulfides (P_4S_3 , P_4S_7 , P_4S_8) and does not exhibit the anomalous viscosity peak common to sulfur and P_2S_5 in the liquid phase.⁽¹⁾

Comparing P_4S_3 to pure sulfur in a binary vapor nuclear power plant will indicate whether phosphorous can be considered as a practical additive. Few of the properties of P_4S_3 are available in the literature and the known parameters (boiling point, molecular weight of vapor, heat of vaporization at normal boiling) are not sufficient to define the thermodynamic properties. AGN measured the heat capacity of liquid P_4S_3 , so that a T-S diagram could be estimated.

Assuming the molecular weight of P_4S_3 to be 195 at the critical point⁽¹⁾ and the liquid density at boiling to be 1.57, the method of Watson gives a critical temperature of 1548°F.⁽²⁾ Van Wazer gives the heat of vaporization at normal boiling to be 139 Btu/lb.⁽³⁾ Heats of vaporization derived from the Clausius-Clapeyron Equation⁽²⁾ using water as a reference (Figure 12), check very well with those calculated for

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- (1) Van Wazer, John R., Phosphorous and Its Compounds, Vol. I, Interscience, New York, 1958, pp 274, 297
- (2) Hougen, O. A. and Watson, K. M., Chemical Process Principles, John Wiley, New York, 1959, pp 67-69, 235
- (3) Private communication, Van Wazer, J. to Sawle, D., February 12, 1960

P_4S_3 HEAT OF VAPORIZATION (WATER REFERENCE)

FIGURE 12.

Figure 13 from Pitzer's acentric factor.⁽¹⁾ The critical pressure is estimated to be 61 atmospheres.

AGN measured heat capacity of the liquid by comparing cooling rates of P_4S_3 and sulfur in the same calorimeter. From this data and the heat of vaporization the rough T-S diagram in Figure 14 was plotted. Van Wazer has evaluated the temperature stability of P_4S_3 ,⁽²⁾ and Figure 15 shows the molecular weight as a function of temperature. Figure 15A shows the vapor pressure as a function of temperature.

II. COMPARISON OF SULFUR AND P_4S_3 CYCLE EFFICIENCIES

The Rankine cycle efficiency approaches the Carnot cycle efficiency as the cycle diagram on the temperature entropy plot becomes closer to a rectangle. The sulfur diagram is far from a rectangle because of the high liquid heat capacity. The P_4S_3 has a lower liquid heat capacity making its diagram more nearly a rectangle. Thus, in operating between a given source and sink temperature, the P_4S_3 will attain a higher cycle efficiency. Another way of considering this is that for a given sink temperature, a lower peak temperature may be used to obtain the same efficiency. An approximate method of considering the magnitude of the effect is to compare values of the quantity:

$$\frac{h_1 - h_2}{h_1 - h_3}$$

where:

- h_1 = enthalpy of saturated vapor
- h_2 = enthalpy after an isentropic expansion to the pressure corresponding to the sink temperature
- h_3 = enthalpy of saturated liquid at the sink temperature.

(1) Pitzer, K. S., Volumetric and Thermodynamic Properties of Normal Fluids, UCRL-8093, January 1958

(2) Van Wazer, op. cit.

P_4S_3 HEAT OF VAPORIZATION FROM PITZER

FIGURE 13.

FIGURE 14.

P_4S_3 TEMPERATURE ENTROPY DIAGRAM

FIGURE 15.

FIGURE 15A.

Sulfur enthalpies were taken from tables in The Sulphur Data Book⁽¹⁾
(improved values of liquid heat capacity are now available from Bureau
of Standards work).⁽²⁾

For comparison purposes a peak temperature of 1200°F and a sink
temperature of 750°F (7.2 psia) have been used. The following enthalpy
values are obtained:

$$\begin{aligned}h_1 &= 418.8 \\h_2 &= 375.6 \\h_3 &= 175.4\end{aligned}$$

The value of h_2 is doubtful due to the changes in average molecular
weight; however, calculations by several different methods at this point
give similar results (i.e., the number of atoms per molecule at state
point 1 is essentially the same at state point 2 so there is little
difference in enthalpies whether or not changes in the number of atoms
per molecule are considered).

$$\text{The value of } \frac{h_1 - h_2}{h_1 - h_3} \text{ is found to be 0.178.}$$

In the case of P_4S_3 , using a sink temperature of 750°F, the data
from Figure 14, and a peak temperature of 1000°F, a ratio of 0.154 was
obtained. With a peak temperature of 1100°F the value is 0.197. This
is an oversimplified approach and the fact that the sulfur is superheated
and at a higher temperature at the turbine exhaust means that the com-
parison is not quite realistic. It does indicate, however, that P_4S_3
with a peak temperature of 1100°F is about equivalent to sulfur with a
peak temperature of 1200°F. To obtain realistic values it would be

(1) Freeport Sulphur Company, The Sulphur Data Book, McGraw-Hill,
New York, 1954

(2) J.A.C.S. 81 29 (1959) West, E. D., "Heat Capacity of S from
25-450°C, Heats and Temperatures of Transition and Fusion"

necessary to make a complete cycle analysis of the two fluids considering feed sulfur (or P_4S_3) heaters, steam superheaters and reheaters, and relative turbine efficiencies.

APPENDIX B
SPECIAL ALLOYS

I. FORD ALLOYS

A family of new alloys was reported by Schmatz* as a means of developing high temperature steels without nickel and chromium to conserve critical materials. The alloys are unique in that they have relatively high percentages of manganese, aluminum and carbon in an austenitic alloy of good ductility and toughness. The 7 to 9% Al and the absence of nickel are the main cause for resistance to sulfur corrosion. The high carbon (0.75 to 1%) does not lead to carbide precipitation effects in view of the high manganese, and the complete absence of strong carbide-forming elements such as Cr, Cb, Ti and others. The high manganese and carbon contents are required to provide a fully austenitic alloy and the excellent mechanical properties as shown in Table B-I. Forging, swaging and hot and cold rolling were all accomplished without difficulty. The first welding test (TIG welding) was completed by Aerojet and was successful. No loss of ductility was noted in the weld. The weld is shown in Figure 16.

Several sample ingots (Heat Z-336-A) were obtained from Ford Motor Company and it was planned to make welded tubing for use in a small natural convection corrosion harp. This was done with very satisfactory results. The welded tube is shown in Figure 17 after being bent to test the weld. A photomicrograph of the weld after the flattening test is shown as Figure 18. The tube shown is approximately 7/8 in. diameter. It was then redrawn to 1/2 in. O.D. tubing. It was planned to weld this tubing into a corrosion harp but this was discontinued pending better understanding of the recent difficulties in the corrosion characteristics.

The cold rolled material of Heat Z-336-A appears to be unstable after prolonged heating at 1200°F. It was originally austenitic and

* Schmatz, D. J., American Society for Metals, Preprint No. 160, November 1959

TABLE B-1

MECHANICAL PROPERTIES OF SELECTED ALLOYS

	ROOM TEMPERATURE			ELEVATED TEMPERATURE 1100 F			1200 F		
	Ultimate Tensile Strength psi	Yield Strength 0.2% Offset psi	% Elongation	Ultimate Tensile Strength psi	Yield Strength 0.2% Offset psi	% Elongation	Ultimate Tensile Strength psi	Yield Strength 0.2% Offset psi	% Elongation
Ford Alloy "E" (30.3 Mn, 7.9 Al, 1.0 C. 1.0 Si)	128,000	78,000	78	90,000	78,000	12	79,000	67,000	18
Ford Alloy "F" (29.4 Mn, 8.9 Al, 1.0 C. 1.4 Si)	121,000	81,000	77	113,000	105,000	10	97,000	78,000	8
Ford Alloy "I" (28.7 Mn, 7.85 Al, 0.78 C. 1.8 Si)	118,000	60,000	75	85,000	70,000	22	---	---	--
AISI Type 316 Stainless (for comparison)	85,500	38,500	60	66,000	20,500	43	56,000	20,000	42
Zirconium 3% Al	129,400	115,800	11.5	68,000	43,000	25	58,000	36,500	32
Zircalloy 2	70,500	40,500	21	18,000	9,000	65	13,200	6,400	80
Carpenter 1JR	86,000	48,000	25	35,000	25,000	45	20,500	12,000	61
Titanium C-120 Av	140,000	130,000	15	62,000	50,000	22	---	---	--

FIGURE 16

Magnification 100x

Nital Etch

Microstructure of Ford Alloy "E" adjacent
to tungsten inert gas fusion welded zone.
No change of hardness was observed.

Weld Ductility Demonstrated by Flattening Test

Elongation of O.D. & I.D.

WELD TEST SAMPLES,
FORD "E" ALLOY

FIGURE 17

FIGURE 18

WELD AND HEAT AFFECTED ZONE OF FORD "E" TUBING
AFTER FLATTENING TEST

Ductility and Hardness were very similar in parent metal and weld deposit.

150X Magnification

Nital Etch

nonmagnetic, but after heating it becomes magnetic forming ferrite and carbides. A photomicrograph of the material in this condition is shown in Figure 5. When fully annealed it may be stable as indicated by the behavior during fabrication of the tubing. A sample of cold rolled Ford Alloy "E" (Heat Z-336-A) is shown in Figure 19. The grain structure after annealing for 10 minutes and for 2 hours at 1900°F is shown in Figures 20 and 21 respectively.

A sample of a similar alloy is called "Langley Alloy" has been obtained from Allegheny Ludlum and it is planned to test it in the near future.

II. ZIRCONIUM-3% ALUMINUM ALLOYS

The 3% aluminum alloys were tested in sulfur without first screening the more common Zircaloy-2 because of the mechanical strength considerations. The aluminum-containing alloys reported by Wagner and Kline* were developed for sodium graphite reactors where their corrosion resistance is equal to most zirconium alloys, but the high temperature strength is much better. The maximum useful temperature from a strength standpoint is above 1250°F, while Zircaloy-2 is limited to about 950°F. Wagner and Kline have reported the physical and mechanical properties, and further work is in process. Various forms including bar, sheet and tubing have been made and no serious problems have resulted. Several of the various modifications, such as additions of Sn and Mo, are also being studied for sodium graphite reactor applications. The properties of selected alloys are shown in Table B-I.

* Wagner, R. K. and Kline, H. E., NAA-SR-3481

FIGURE 19

Magnification 250x

Elect. Etch

Cold Rolled Ford Alloy "E"

Heat Z-336-A 5% H_2SO_4

FIGURE 20

Magnification 250x

Elect. Etch

10 min. annealed - 5% H_2SO_4
at 1900°F

FIGURE 21

Magnification 250x

Elect. Etch

2 hour annealed - 5% H_2SO_4

at 1900°F