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MASTER

LITHIUM STUDIES

- METALLURGICAL AND CHEMICAL EVALUATIONS OF A TEST FACILITY AFTER 2000 HOURS OPERATION
- HYDROGEN ISOTOPE MONITORING IN LITHIUM
- LITHIUM AEROSOL FORMATION IN RELATION TO FUSION REACTORS

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CONTENTS

Section I, Parts 1 and 2

- Metallurgical and Chemical Evaluation of a Test Facility after 2000 hours Operation

The Experimental Lithium Facility, ELF, was operated for two thousand hours with main loop containment temperatures ranging from 390° to about 550 °C. During this period, weight change data were obtained at 538 °C for several austenitic and ferritic alloys for up to one thousand hours of exposure. The general conclusion drawn from this relatively short exposure was that in terms of weight loss the corrosion of austenitic alloys was a factor of three more severe than the ferritic materials.

The present study was undertaken in an attempt to learn more about the characteristics of lithium corrosion. Part one of this report deals with a metallographic evaluation of the Type 304 Stainless Steel one-inch tubing, used for the main loop containment, and gives a detailed account of hot leg and cold leg corrosion. An examination of the dump tank was also conducted in order to determine why lithium was apparently "creeping" from the tank during loop operation and forming a plug in the cover gas line.

Part two is a detailed chemical evaluation of the hot trap and the cold trap, performed in order to gain some measure of component design, trap efficiency and the migration of corroding species.

Section II

- Hydrogen Isotope Monitoring in Lithium

Development work is reported on two alternative techniques for the determination of dissolved hydrogen in liquid lithium. The permeation-type sensor with a niobium membrane was shown to respond well to hydrogen concentration changes and provides a continuous, on-line readout. Thermodynamic calculations have also shown that equilibration of lithium with yttrium foil and subsequent analysis of the foil for hydrogen can provide a periodic calibration check for such on-line meters.

Section III

- Lithium Aerosol Formation in Relation to Fusion Reactors

Results are presented concerning the magnitude of lithium aerosol formation in both helium and argon atmospheres as well as under partial vacuum conditions. The impact such aerosols will have on the use of lithium in fusion power reactor technology is discussed, and particular note is made of the important effect of sodium impurities in the liquid lithium.

Appendix (Published Paper)

- Materials Behavior in Lithium Systems for Fusion Reactor Applications

SECTION I: Metallurgical and Chemical Evaluation of a Test
Facility after 2000 Hours Operation

Part One: Metallurgical Evaluation
C. Bagnall

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PART ONE: METALLURGICAL EVALUATION

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SECTION I: Metallurgical and Chemical Evaluation of a
Test Facility after 2000 Hours Operation

Part Two: Chemical Evaluation
Z. L. Kardos and C. Bagnall

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PART ONE: METALLURGICAL EVALUATION

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1.0 OBJECTIVES

The primary objective of this study was to determine how well the T 304 SS 2.5 cm diameter containment tubing withstood the two thousand hour exposure to lithium at 550°C. This examination, while necessarily qualitative from a corrosion standpoint, was aimed at revealing the nature and degree of attack, the effects of downstream position, and the reaction of the liquid metal at welds and weld heat-affected zones.

Since it was intended to re-use the 4 meter long economizer in a new lithium facility, examination of the colder, deposition regions of the loop was restricted to the temperature zone below 400°C. A secondary objective here was to determine the composition and nature of deposited material and to also examine metallurgical effects at weld regions.

In addition to the above studies, it was decided to cut open the dump tank in order to determine the cause and severity of the apparent "creeping" phenomenon that resulted in repeated blocking of the argon cover gas line which ran from the top of the dump tank.

2.0 AS-RECEIVED CONTAINMENT TUBING

The main loop of ELF was constructed with 2.5 cm diameter 304 SS seamless tubing (1.000" OD, 0.065" min. wall). The material was cold drawn, annealed in accordance with SA 213 (1040°C min/30-60 minutes per inch thickness + WQ) and pickle cleaned. The nominal material chemical composition is given in Table I below:

TABLE I
Nominal Chemical Composition of 2.5 cm Diameter T 304 SS Tube

Heat No.	C	S	P	Mn	Si	Cr	Ni	Fe
93104	0.065	0.02	0.03	1.7	0.3	18.65	8.11	R

The microstructural appearance of the tube wall at the ID and the ID surface is shown in Figure 1. A longitudinal section revealed a grain size of ASTM 6. The material contained numerous inclusion stringers but was otherwise devoid of second phase precipitation. The inner tube surface was clean but exhibited some irregularity from grain to grain. Additional examination on the SEM [Figure 1(b), (c)] revealed that this was a result of the pickling operation; some areas of the tube surface were etched more heavily than others. The chemical composition obtained by EDAX (Energy Dispersive Analysis by X-Ray) from the unexposed tube ID and from the mid-wall region of exposed tubing is given in Table II.

TABLE II
Chemical Composition from the Surface and Mid-Wall
Region of 2.5 cm Diameter T 304 SS Tube (EDAX)

	Fe	Mn	Cr	Ni	Mo	Cu	Al	Si	Ca	S
AR Inside Surface	68.6	1.4	19.0	8.3	0.4	0.3	N/A	N/A	N/A	N/A
Exposed Mid-wall	66.1	2.3	20.8	7.9	N/A	N/A	0.5	0.8	0.1	0.1

N/A: Not Analyzed

3.0 HOT LEG CONTAINMENT

3.1 Cross Section Metallography

Sections cut from the ELF containment are identified in Figure 2 with location, temperature and descriptive details given in Table III. Specimens #1 through #8 cover the hot temperature regions of the system from about 530° to 550°C. Although this zone of the loop was about 7.5 meters in length and contained two banks of clamshell heaters, the entire section operated under

100 μ m

a). Surface structure

20 μ m

b). Surface structure

20 μ m

c). Longitudinal section — inside wall.
Etch: 6 Glycerol/5 HCl/4HNO₃

Figure 1 — Microstructural appearance of 2.5 cm diameter T304SS tube wall at the inside surface.

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Figure 2 — Schematic of the experimental lithium facility, (ELF), showing location of specimens cut from the containment.

TABLE III
ELF Loop Specimen Data

Specimen Number*	Distance from Test Leg		Temperature		Description	C	W	E	T
	Inch	Cm	°F	°C					
1	0	0	990	530	Hx exit: straight section	X			
2	26	66			Middle of 1 st Htr. leg	X			
3	57	145			Elbow	X	X	X	
4	82 1/2	209			Middle of 2 nd Htr. leg	X			
5	96 1/2	245			Exit of Htr. (L/D = 0)	X	X	X	
6	129	328			Tee joint	X	X		X
7	202	513	1000-1020	540-550	Straight section	X			
8	302	767	1020	550	Ht. inlet: Straight section	X	X		
**9	152	386	750	400	Straight section	X	X		
10	205	521	735-745	390-395	Elbow at cooler exit	X	X	X	
11	275	698			Tee at pump exit	X	X	X	
12	324	823	735	390	Straight section before Hx	X			

Notes: *See Figure 2 for loop location of each specimen.

C: Containment Tube

W: Weld

E: Elbow } Forgings

T: Tee }

**Distances measured for 9 thru 12 measured from specimen 8.

near-isothermal conditions. The major portion of the temperature change (and heat exchange) in the loop occurred in the 3.7 meter-long economizer with temperatures at the two ends being $\sim 550^\circ$ (Spec. #8) and 390°C (Specimen #12).

Figure 3 shows the cross-section microstructure of the containment tube at the lithium exposed surface for Specimens #1 and #2 ($\sim 530^\circ\text{C}$). The base metal exhibited a characteristic structure for annealed tubing exposed at this temperature for 2000 hours. Grain boundary carbide development was well advanced with near continuous growth evident in the majority of boundaries. The lithium affected zone, about $20\text{ }\mu\text{m}$ deep, was porous and inhomogeneous. The most striking feature was perhaps the fact that the interface between the base metal and the reaction zone, unlike sodium-exposed material, was irregular and did not have the appearance of a diffusion interface. There was no indication of accelerated leaching at grain boundaries - but otherwise the structure looked as though it was at an early stage in the development of an equilibrium condition. The main loop flow rate in ELF was about $1.04 \times 10^{-4}\text{ m}^3/\text{s}$ (1.65 gpm), giving a velocity of only 0.27 m/s (0.89 fps) through the one-inch containment tube. This factor may account for the observed effects since the time to equilibrium at this velocity may be on the order of $10^4 - 10^5$ hours.

In Figure 3(b), details of the surface zone microstructure are more clearly evident at the higher magnification. The porosity (black spots) is considerable but generally spherical and small in size, ranging from about 0.2 to $2.0\text{ }\mu\text{m}$ in diameter. The pore density is greatest at the surface zone: base metal interface, rather than at the liquid metal surface. Pore size, however, increases with distance from the interface.

Within the surface zone, [Figure 3(b)] the formation of a new grain structure was observed. The structure is not clearly defined at this stage but consists of ferritic grains, generally smaller than $5\text{ }\mu\text{m}$ diameter, with a few islands of original austenite still undergoing the process of dissolution and transformation. The basic ferritic nature of this surface layer is examined in more detail in a later section.

a). Location #1
Etch: 5% chromic acid.

20 μ m

← Ni plate

b). Location #2
Etch: 5% chromic acid.

5 μ m

Figure 3 – Containment tube microstructure: Locations # 1 and # 2.

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Further downstream at location #5 [Figure 4(a), (b), (c)], the lithium-affected zone appears even more irregular. In the unetched micrograph [Figure 4(a)] the porosity is very clear with pore density greater at the ferritic: austenitic interface, but pore size again greater towards the liquid metal surface. The considerable variation in thickness of the depleted zone at this location is more evident than at positions further upstream. In addition, pronounced notches and undulations were noted at the corroded surface itself - in contrast to the very even character revealed in Figure 3.

Figure 4(c) shows a section taken from a forged elbow at location #5. Apart from a difference in grain size, all other features were similar to those observed on the tubing.

At the most extreme downstream position, location #8, shown in Figure 5(a) and (b), the irregular ferritic: austenitic interface is closely matched by - but not related to - a pronounced notching of the lithium exposed surface. The porosity, however, no longer spreads throughout the reaction zone but is confined to the lower region and is separated from the surface by a solid layer of 5 μm diameter grains.

3.2 SEM & EDAX

All specimens used for scanning electron microscopy were cleaned and stored in methanol in order to preserve the corroded surface. Prior to examination in the SEM, each specimen was placed in fresh alcohol and ultrasonically cleaned.

Figure 6 compares the surface appearance of specimens from locations #1, #4, and #5. Three basic features are evident:

- o A new, very small ($\sim 5\mu\text{m}$) equiaxed grain structure. The equiaxed form, deduced from SEM and optical micrographs, is different from the columnar growth of ferritic layers observed in sodium exposed alloys. The fine equiaxed structure appears to be a typical, stable lithium corrosion feature, and is not affected by alloy type, surface

a). Tube (unetched)

b). Tube (etched)
Etch: 5% chromic acid

c). Elbow (etched)
Etch: 5% chromic acid

← Ni plate

Figure 4 – Containment microstructure: Location # 5.

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Ni plate

a). Unetched, showing porosity in the surface reaction zone.

20μm

Ni plate

b). Etched; 5% chromic acid.

20μm

Figure 5 – Containment tube microstructure: Location # 8.

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a). Location #1

b). Location #4

c). Location #5

Figure 6 – Containment tube surface (S.E.M.): Locations # 1, # 4 and # 5.

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condition or downstream position. A similar structure was observed by Whitlow et al.⁽¹⁾ on heavily worked 2-1/4Cr-1Mo, after only 200h/538°C, at a velocity of 1.8 m/s. (See also Figure 2, Part 2.)

- o A decrease in surface porosity as a function of downstream position. In Figure 6(a), the small pores, 2-4 μ m in diameter and located at the new grain boundaries, account for about 20-30% of the exposed tube surface. Moving downstream, the porosity decreases rapidly [compare Figures 6(a), (b), & (c)].
- o An increase in surface topography as a function of downstream position. The very flat, porous surface at location #1 gives way to large undulations separated by deep ravines of localized corrosion at location #5.

The two latter effects are illustrated further in Figure 7(a), (b), and (c); porosity at these two locations (#7 & #8) is now virtually absent, but the ravines of Figure 6(c) have turned into canyons, which separate large, relatively flat, grain-like blocks from one another. This structure owes its origin to the prior austenite microstructure, but after initial highly selective attack at the grain boundaries, has developed to the present morphology. The surface "blocks" are in the 20-40 μ m diameter range--somewhat smaller than the original base metal grain size. The early development of this downstream surface structure can be seen on the inside wall of the hot trap containment (Figure 2, Part 2). The total exposure here is only 216 hours at 538°C, but already this striking feature of lithium corrosion is evident.

A plot of porosity vs. downstream location is shown in Figure 8. The curves represent estimates only, but the plot does show graphically the rapid decline in surface porosity, while at the interface region it remains relatively constant, ranging between 10 and 30%. It should be noted that this micro-porosity is difficult to observe in etched cross-section samples and difficult to evaluate for certain in unetched specimens because of factors, such as flowed metal or polishing compound embedded in the pores. However, regardless of the actual volume fraction of porosity, it is present - in a significant amount - from one end of this hot leg to the other.

a). Location #7

20 μ m

b). Location #7

10 μ m

c). Location #8

10 μ m

Figure 7 — Containment tube surface (S.E.M.): Locations # 7 and # 8.

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Figure 8 — An estimate of porosity change in the surface zone of containment tubing after 2000h exposure to flowing sodium.

The source of the sub-surface porosity - particularly where it is apparently sealed from the lithium interface at downstream locations - is not so readily explained. In view of time and temperature considerations, it is unlikely to be a diffusion-related phenomenon, and may well be explained as the result of a leaching reaction. If this is indeed the case, it would be necessary to postulate some sort of lithium ingress along the austenite: ferrite boundary, with only limited access to the lithium mainstream.

In the absence of weight change data, it is difficult to assess the relative change in severity of mass loss along this 800 cm leg. The high surface porosity upstream (and consequently the large surface area) would suggest that corrosion is taking place more rapidly at this location than further downstream. The depth of the lithium-affected zone remains relatively constant at about 20 μ m along the leg.

There is some evidence to suggest that this depth is a function of velocity. The 1000-hour weight change specimens from the earlier studies in ELF revealed that the reaction layer for several different alloys, including T 304 SS, was on the order of 5 μ m.⁽¹⁾ The lithium velocity in this section of the hot leg was 1.8 m/s.

With more data, a correlation may eventually be established linking equilibrium depth of the reaction zone to one or more of the major variables governing lithium corrosion rate (e.g., nitrogen content, velocity, loop ΔT and temperature). The velocity parameter, in particular, requires further study over the 0-7 m/s range to determine its influence on rate of mass loss.

The low velocity conditions over the surface of the ELF containment may be largely responsible for the absence of any significant chemical downstream effect. The surface composition changes along the 800 cm leg were surprising, both for their uniformity and their lack of severity - as shown in Table IV below. Nickel depletion in particular was considerably less than anticipated - in view of its high solubility in liquid lithium.

TABLE IV
Surface Composition Changes Along
the Hot Leg Containment of ELF

<u>Location</u> #	<u>Dist. from Hx.</u> (cm)	<u>Fe</u> (%)	<u>Cr</u> (%)	<u>Ni</u> (%)
Base Metal	-	66.0	21.0	8.0
1	0	88.5	7.0	1.5
4	209	87.0	9.0	1.5
5	245	84.0	9.5	3.0
7	513	85.5	10.5	1.0
8	767	85.5	10.5	1.0

Note: o 2000 hour exposure, 530° - 550°C.
 o T 304 SS, 1 inch diameter x 0.065 inch wall tube.
 o SEM/EDAX data from inside surface (base metal composition from center wall); constant count rate (Fe ref) give data $\pm$ ~1%.

The data recorded by Whitlow et al., in the higher velocity isothermal test leg, positioned between locations #5 and #7, show that after 1000 hours there is a significant downstream effect in terms of weight loss. For example, T 304 SS dropped from a corrosion rate of 37 μ m/y to 29 μ m/y within 15 cm. The 1000-hour surface chemistry (SEM/EDAX) for T 304 SS was reported as 84.1 Fe, 8.9 Cr, 2.9 Ni, showing very close agreement with the 2000-hour low velocity containment results. No surface porosity was noted in these specimens.

Several conclusions may be drawn from these observations:

- o Lithium corrosion at 540°C produces very rapid surface chemistry changes, which remain constant over long time intervals (200-2000h) and appear to be relatively independent of lithium velocity (0.2 to 2.0 m/s) and downstream position.

- o There is a significant downstream effect in terms of weight loss (1000h data).
- o There appears to be a distinct effect of lithium velocity on the depth of the reaction (or depletion) zone. At higher velocity, (2 m/s), the zone depth is 4 μ m after 200h - and about 5 μ m after 1000h at 540°C. At lower velocity (0.2 m/s), the zone depth is 20 μ m after 2000h and independent of downstream position (0-800 cm).
- o Porosity in the reaction zone appears to be a prominent feature for T 304 SS. Porosity is always present at the austenite: ferrite interface but is strongly dependent on downstream position for its presence on the lithium exposed surface. The mechanism for pore formation appears more linked to lithium leaching in the reaction zone than to diffusional effects.
- o The disappearance of surface porosity at downstream locations, while not understood, seems to be linked to a change in the severity of lithium attack. At upstream locations a flat, very porous surface - indicating general attack - gives way to a sharply creviced topography with no porosity, suggesting more localized corrosion.

3.3 Weld Zone Evaluation

Three welds were examined in the hot leg section of ELF. As shown in Figure 9(a), (b) and (c), there was no evidence of any change in mode of attack in the reaction zone at the weld heat-affected zone or on the weld metal itself.

The fact that lithium corrosion in T 304 SS at 540°C is unaffected by microstructure or heat treatment is an important finding. It appears that the rate and degree of interaction of lithium, containing about 100 ppm nitrogen, with the surface is simply governed by basic alloy chemistry. Factors, such as a cast, wrought or heavily worked surface microstructure - or the presence or absence of second phases (such as weld metal, δ -ferrite, or grain boundary carbide), - seem to have no influence. The corrosion reaction rapidly proceeds to a fixed depth, (possibly dependent on velocity) and

Figure 9 – Cross sections of welds in the hot leg of E.L.F.

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removes alloy constituents by leaching. Diffusional processes, at least for the first two thousand hours of exposure, seem to be playing a very secondary role.

Some support was gained for the above hypothesis by reviewing the metallography conducted on test materials exposed for 1000h at 538°C in the earlier loop experiments. All the austenitic materials (T 304, 316, 321 and 347 SS) produced porous zones while the ferritic alloys (2 1/4Cr-1Mo, 9Cr-1Mo) did not. This evidence underscores the predominant role played by nickel in the lithium corrosion reaction and suggests also that the amount of chromium present has a relatively small effect.

Surprisingly enough, as already indicated for T 304 SS in Table IV the "equilibrium" surface nickel content does not drop to zero. In liquid sodium, this is not the case: all alloys move towards a composition of 95 + % Fe, 2-3% Cr, 0% Ni.⁽²⁾ Table V shows data compiled for various materials exposed in ELF. Although these results cannot be interpreted at present in terms of an equilibrium condition, they do point out a clear direction towards which the activity is driving each major alloy component in the system.

TABLE V
Surface Analysis of Various Materials After
Exposure in ELF at ~540°C (EDAX)

<u>Material</u>	<u>Exposure (Hr.)</u>	<u>Composition (%)</u>		
		<u>Fe</u>	<u>Cr</u>	<u>Ni</u>
T 304 Containment -weld metal at #5	2000	84.0	9.5	3.0
T 304 Corrosion Spec.	1000	84.0	9.0	3.0
T 304 L Corrosion Spec.	1000	85.0	9.5	2.5
T 316 Corrosion Spec.	1000	83.0	10.5	3.0
*(AR) 2 1/4Cr-1Mo Corrosion Spec.	1000	88.5	6.0	2.5
*(AR) 9Cr-1Mo Corrosion Spec.	1000	87.5	7.0	2.0

*AR: As-received (normalized & tempered)

If Table V can be interpreted as an approach to the equilibrium condition from two directions, then it appears that surface equilibrium will be reached very rapidly and, for the basic temperature and lithium chemistry conditions represented by ELF, the equilibrium surface composition will be approximately 85 Fe, 8 Cr, 3 Ni. Manganese, whose corrosion behavior as an alloy constituent (in sodium and in lithium) follows that of nickel, will probably account for the majority of the remainder.

This brief examination of welded areas in the hot leg in conjunction with data obtained earlier leads to the following conclusions:

- o With a moderate concentration of nitrogen (~ 100 ppm), lithium corrosion of T 304 SS is not influenced by microstructure, thermal history, fabrication method or surface condition, but is governed by basic alloy composition.
- o Although nickel plays a predominant role in the interaction of lithium with a metal surface, it is not depleted entirely from nickel-bearing alloys. The presence of nickel in the austenitic materials leads to porosity in the reaction zone.
- o Corrosion of ferritic alloys is about a factor of three lower than austenitics at 538°C . The influence of compositional variations appears small, but a heat treatment maximizing stable carbide precipitates (M_{23}C_6) while minimizing Fe_3C is beneficial. The surface chemistry of ferritic alloys gains 2-3% Ni when exposed in an austenitic loop.
- o An examination of the relatively short-term data available for austenitic and ferritic alloys indicates that an equilibrium hot-leg (538°C) surface composition for a lithium AT system will be 85 Fe, 8 Cr, 3 Ni, with 1-3% Mn.

4.0 COLD LEG CONTAINMENT

Three locations from the cold leg are discussed in this section. Two facts emerged; the dominant element in the surface deposits was nickel (the Cr-rich zone presumably being further upstream in the economizer) and that even this lowest temperature region was not entirely free of corrosive attack.

4.1 Location #10; Containment Tube After Finned Cooler

The cross-section micrograph [Figure 10(a)] shows that, after passage through the finned cooler and the final temperature drop from 400°C at the heat exchanger exit to about 390°C, the deposition rate is still relatively high. The deposit remaining after alcohol cleaning measures about 2-3 μ m in thickness and appears to uniformly cover the tube surface.

The SEM micrographs [Figure 10(b), (c)] show that the deposit is composed of a conglomeration of crystallites. The impinging growth of individual crystals has resulted in the formation of an open deposit structure. Spot analysis on the crystals produced a basic composition of 36.5 Fe, 2.0 Cr, 54.0 Ni, 4.6 Mn.

4.2 Location #11; Welded Tee at Flowmeter Exit

The welded tee, not shown on the schematic in Figure 2, was used in order to make a sharp, space-saving bend in the containment tubing. The temperature at this tee was again about 390°C. Figures 11(a) and 11(b) show a significant change in deposition surface character, approximately 180 cm downstream from location #10. Porous, uneven and relatively thick deposits can be seen in the vicinity of the weld heat-affected zone, where the weld underbead has formed a protuberance in the lithium flow channel. Further away from the weld, deposit thickness is not measurable; and there is a marked notching at grain boundaries, indicating a degree of selective corrosion during the 2000h exposure. At higher magnification, Figure 11(c), it seems clear that preferential grain boundary attack has taken place with the loss of some grains. This conclusion is supported by a comparison of this figure with the surface profile of as-received tubing, shown in Figure 1 (c).

Ni plate

Deposit

- a). Cross section
Showing 2-3 μ m thick deposit
Etch: 6 Glycerol/5 HCl/4 HNO₃

20 μ m

- b). Surface features (SEM)

10 μ m

- c). Surface features (SEM)

2 μ m

Figure 10 – Deposit formation: Location # 10.

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Figure 11 – Longitudinal cross sections of containment tubing at a welded tee: Location # 11.

4573-16

4.3 Location #12; Containment Tube at Heat Exchanger Inlet

This location is at the end of the cold leg, again at 390°C and some 823 cm from the hot end of the heat exchanger (location #8) where temperature drop and deposition processes begin. Cross-section metallography of the tubing [Figure 12(a)] again showed a very thin deposit superimposed on a corroded surface with attack sharply accentuated at grain boundaries. This phenomenon is clearly illustrated in Figure 12(b) where the austenitic grains appear demarcated under a thin film of deposit.

Closer scrutiny of the deposit [Figure 12(c)] revealed that it was a very open, sponge-like structure, with EDAX spot analysis giving a composition of 40.5 Fe, 3.0 Cr, 47.0 Ni, 6.0 Mn. The only noteworthy change from location #10 - apart from the distinct difference in deposit growth character - is the increase in Mn at the expense of Ni, with downstream position.

5.0 DUMP TANK EXAMINATION

During the course of the 2000h operation of ELF, several occasions arose at which the cover gas supply to the dump tank was cut off by the formation of a lithium nitride plug in the cover gas line. Each time, the plug formed just above the dump tank in 1.25 cm diameter inch tubing and had to be drilled out. This procedure was by no means without difficulty since the plug had the consistency of cement and offered considerable resistance to the hardened steel drill bit.

No satisfactory explanation was forthcoming regarding a mechanism which would explain this behavior. At 300°C the vapor pressure of lithium is on the order of 10^{-6} torr so that vapor deposition seems impossible. The observation of liquid metal "creep" up the sides of a containment vessel is usually associated with the presence of large impurity concentrations or a second, immiscible liquid, such as a molten salt.

Ni plate

Thin deposit

a). Note thin deposit
Etch: 6 Glycerol/5 HCl/4 HNO₃

20μm

b). Surface features (SEM)

20μm

c). Surface features (SEM)

2μm

Figure 12 – Deposit formation: Location # 12.

4573-17

A decision was made to cut one end off the dump tank without draining the lithium in order to look at the inside surfaces as they were during operation. The 25 cm diameter pipe cap was removed using a manual pipe-cutter. In this way, the temperature of the cut was kept very low. The lithium metal, occupying about one third of the tank volume in its solid state, was separated at the cut with a chisel.

A photograph, taken immediately after the tank interior was exposed, revealed the lithium surface and much of the tank interior coated in a thin layer of brick-red nitride (Figure 13). The ceiling of the tank was splattered with frozen droplets and a "tide-mark" was clearly discernable about 4 cm above the solidified metal surface. This tide-mark extended around the walls of the tank, around the fill line (foreground) and the level probe well at the rear of the tank. In between these two penetrations was a third "pipe", also extending to the liquid metal interface. This artifact turned out to be a hollow "stalactite" primarily of lithium nitride. It was friable, black inside and of a cindery consistency and must have formed during the original lithium fill operation, which took place through the cover gas inlet to the tank. The combined effect of a relatively slow pouring rate, a low temperature and some gas impurity must have resulted in the growth of this cinder pipe which clearly provided a path for lithium transfer from the tank to the cover gas line during pressure change events, such as loop dump and fill operations.

6.0 CONCLUSIONS

The metallurgical evaluation of ELF containment and a review of corrosion data obtained earlier from austenitic and ferritic alloys exposed at 538°C led to the following major conclusions:

- o Lithium corrosion at 538°C produces very rapid surface chemistry changes which are independent of velocity and downstream position.
- o There is a significant downstream effect in terms of weight loss.

Figure 13 — E.L.F. dump tank interior (25 cm diameter pipe).

4573-18

- o The surface reaction zone depth is related to lithium velocity.
- o Porosity in the reaction zone is a prominent feature for austenitic alloys.
- o With moderate nitrogen impurity concentrations in the lithium, corrosion of austenitic alloys is primarily governed by alloy composition and is not influenced by microstructural, mechanical working or thermal history factors.
- o Corrosion of ferritic alloys is about a factor of three lower than austenitics at 538°C. The influence of composition appears small, but heat treatment effects are significant.
- o For an austenitic lithium containment, the equilibrium composition for the corroding area of a ΔT system is about 85 Fe, 8 Cr, 3 Ni, with 1-3% Mn.
- o In the furthest downstream locations of the colder regions of the loop, nickel dominates the deposit formations.
- o Preferential grain boundary corrosion of austenitic alloys was evident in the colder zone. This phenomenon may only be active during the early stages of system operation, and, in the absence of wall thinning data, its significance could not be estimated. There was no indication that this corrosion would eventually lead to a more severe, penetrating condition that might be classified as intergranular attack.
- o The problem of plug formation in the cover gas line was found to be due to lithium suction up a "tube" of lithium nitride, and not due to lithium creep at 300°C.

The above results were obtained in a test loop with a ΔT of about 150 Celsius degrees, and with a nitrogen content in the lithium of about 100 ppm (oxygen concentration was also close to this level). Further studies are required to clarify the role played by the basic parameters that influence the corrosion mechanism before predictive equations relating these variables can be formulated.

7.0 ACKNOWLEDGEMENTS

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*See Appendix

PART TWO: CHEMICAL EVALUATION

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1.0 OBJECTIVES

In order to obtain the maximum amount of information about the reactions of liquid lithium within an austenitic ΔT system, an extensive chemical evaluation of the ELF hot trap and cold trap was undertaken. The work encompassed a study of the trap components and containment alloys, the getter materials, deposits and residual lithium. The prime objectives were to establish quantitative data for the chemical and physical reactions occurring within the traps and to assimilate sufficient information to permit the design of more efficient lithium chemistry control systems.

2.0 The Hot Trap

The hot trap operated for only three brief 72-hour periods at 538°C throughout the 2000 hours of total loop operation. The trap subloop was isolated without flow for the remaining interval.

At the time of removal from ELF, the hot trap inlet and exit lines were found to be drained of all but a residual wetting coat of lithium metal. The trap was cut as indicated in Figure 1, and the lithium coated internals were cleaned by aqueous dissolution. All components, hot trap container wall, zirconium foils, titanium foils and the aqueous solution, were held for analytical examination.

2.1 Trap Geometry

The hot trap consisted of a 23cm long T304SS tube with an inside diameter of 5cm. Lithium entered via a 1.3cm dia tube (0.5 in. dia. x 0.049 in. wall) joined to the center of one end cap, flowed through the coiled getter foils

Figure 1 — Schematic diagram of ELF hot trap.

and out through a similar tube at the other end. Lithium mass flow rate averaged about $4.3 \times 10^{-3} \text{ m}^3/\text{sec}$ (0.68gpm).

2.2 Trap Analysis

The interior hot trap wall gave the appearance of a finely abraded surface and had a bright silver sheen. A section of wall material was removed for scanning electron microscopy and x-ray analysis.

Two rolls of alternately wrapped getter foils were fabricated for the hot trap. One foil was corrugated, the other flat. Spring tension in the rolls resulted in the outermost turn of flat foil being pressed against the containment wall. Despite this protection, significant surface changes were noted on the T 304 SS as shown in Table I below:

TABLE I
T 304 SS Hot Trap Containment Surface Composition
(X-Ray Analysis)

COMPOSITION %	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Ni</u>	<u>Cu</u>	<u>Mo</u>
Exterior Wall Air Exposed 538°C/216 hr.	18.9	1.54	66.4	10.2	0.15	0.25
Interior Wall Li Exposed 538°C/216 hr.	15.4	1.79	75.7	5.7	0.06	0.28

Figure 2 shows the appearance of the lithium exposed surface; the small cell-like structures, typical of lithium corrosion, are present together with evidence of selective attack at the austenitic grain boundaries.

2.3 The Getter Foils

Two identical rolls of foil, each 9.5 cm long, were located in the hot trap pipe. Each roll consisted of alternate layers of corrugated zirconium and flat titanium. The packing was such that the flow path was more open towards the center of the roll.

a). Surface features (SEM)

100 μ m

b). Surface features (SEM)

10 μ m

Figure 2 — Lithium exposed containment wall of the hot trap.

4573-2

Analysis of the two foil materials is divided into physical changes, non-metallic and metallic impurity pickup and SEM data.

2.4 Zirconium Foil Getter

2.4.1 Physical Changes

The 9.5cm wide zirconium foil was formed with 6mm corrugations and a 2mm radius on the bend. A comparison of physical parameters before and after exposure is given in Table II.

TABLE II

Zirconium Foil: Physical Parameters

	<u>As Received</u>	<u>Li exposed (216h/538°C)</u>
Foil Thickness	84 μ m	104 μ m
Physical Appearance	Shiny and Flexible	Dull and Brittle
Color	Tarnished Gray Gold	Black
Area Used in Trap	-----	1980cm ² (Corrected for Corrugation)
Zr Foil Wt. Per Sq. Cm	0.0560g	Not measured
No. of turns per roll	-----	5 (two rolls in trap)*

*Note: The 5th zirconium turn was the inner-most (center) turn and was not separated by a titanium foil from the 4th. This packing arrangement was required to fill the center spacing of the hot trap.

2.4.2 Non-Metallic Impurity Analysis

Analysis for hydrogen, oxygen and nitrogen was determined by high temperature vacuum extraction followed by gas mass spectrometry. The values reported represent total gas release from the foils including any adhering chemical compounds remaining on the metal surface. No attempt was made to remove surface corrosion products after initial aqueous dissolution. The analytical data are given in Table III and show only moderate pickup for all three elements. This finding is in qualitative agreement with Weston et al.⁽¹⁾

TABLE III

Zirconium Foil: Non-Metallic Impurity Analysis
(Hot Trap - 216h/538°C)

	Gas Content (ppm)		
	<u>Hydrogen</u>	<u>Oxygen</u>	<u>Nitrogen</u>
Unexposed	15	1269	<100
Inlet (av.)	174	3124	1724
Outlet (av.)	178	3509	1826
Average for exposed foil	176	3316	1775

2.4.3 Metallic Impurity Analysis

Selected sections of zirconium foil representing inlet and outlet zones of the hot trap were analyzed by x-ray fluorescence. Elemental intensities of each element found are given in Table IV. Clearly, there has been some gettering of Ni in particular, and also Ca which was present as an impurity in the lithium. Again, this is in agreement with work in Ref (1).

TABLE IV

Zirconium Foil: Metallic Impurity Analysis
(Hot Trap - 216h/538°C)

	Impurities (x-ray intensities - counts per second)				
	<u>Ca</u>	<u>Ti</u>	<u>Cr</u>	<u>Fe</u>	<u>Ni</u>
Unexposed Foil	126	81	508	737	548
Inlet Zone (av)	423	169	546	1326	6365
Outlet Zone (av)	419	254	553	1832	5859

Note: Data are averages for five specimens.

2.4.4 SEM Examination

The surface of the zirconium foil before and after exposure in the hot trap is shown in Figure 3(a) and (b). There is clear evidence of rolling damage on the unexposed foil, but little or no effect of the lithium exposure to be seen, other than a general surface etching. A marked structural directionality is still evident and there are some crystalline deposits adhering to the surface after the cleaning operation. The nature of these deposits was not studied further. X-ray data, however, indicated that the nickel picked up by the foil was not confined to these particles.

2.5 Titanium Foil Getter

2.5.1 Physical Changes

The titanium foil was manufactured as 9.5 cm wide strip. It was wrapped into a roll with the corrugated zirconium foil and formed a spacer between the corrugated layers. A comparison of physical parameters before and after exposure is given in Table V.

TABLE V
Titanium Foil: Physical Parameters

	<u>As Received</u>	<u>Li exposed (216L/538°C)</u>
Foil Thickness	41 μ m	84 μ m
Physical Appearance	Shiny - Flexible	Dull - cracked under stress
Color	Silver	Tan Gold
Area Used in Trap	-----	1161cm ²
Ti Foil Wt. Per Sq. Cm.	0.0193g	0.0211g
No. of Turns per Roll	-----	4

a). Unexposed

10 μ m

**b). Exposed: 538°C/216h
(Exit region of trap)**

10 μ m

Figure 3 – Zirconium foil surface characteristics (SEM).

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2.5.2 Non-Metallic Impurity Analysis

The gas analysis method was identical to that used for the zirconium foil. Again, the reported values for hydrogen, oxygen and nitrogen represent the total gas release from the metal as well as from residual surface contamination. The analytical data are given in Table VI. The striking feature of these results is the large increase in nitrogen concentration. The increase is an order of magnitude greater than for the zirconium foil.

TABLE VI
Titanium Foil: Non-Metallic Impurity Analysis
(Hot Trap - 216h/538°C)

	Gas Content (ppm)		
	<u>Hydrogen</u>	<u>Oxygen</u>	<u>Nitrogen</u>
Unexposed	95	2519	184
Inlet (av.)	133	3759	13376
Outlet (av.)	89	3260	15624
Average for exposed foil	111	3509	14500

2.5.3 Metallic Impurity Analysis

The x-ray fluorescence intensity analysis provides an indication of the elemental impurities retained on the foil surface after aqueous dissolution and washing in demineralized water. The data are given in Table VII. Note that the major difference between the Ti and Zr foil is in the amount of Ni retained. At 6000 ppm, the Zr has removed twice as much from the lithium as the titanium. It is of interest to note that a significant quantity of Zr has been transferred to the Ti.

TABLE VII
Titanium Foil: Metallic Impurity Analysis
(216h/538°C)

	Impurities (X-ray Intensities - counts per second)			
	<u>Zr</u>	<u>Cr</u>	<u>Fe</u>	<u>Ni</u>
Unexposed Foil	731	278	801	377
Inlet Zone (av)	1462	623	1920	3292
Outlet Zone (av)	2550	307	1384	2807

Note: Data are averages for three specimens.
Ca not detected on Ti foil.

2.5.4 SEM Examination

The surface of the titanium foil before and after exposure in the hot trap is shown in Figure 4 (a) and (b). The foil was highly fissured in the unexposed condition. Titanium has an hexagonal crystal structure up to 882°C and a body centered cubic lattice above this temperature to the melting point at 1660°C. Forming operations, such as rolling to thin foil, are thus different.

After exposure [Figure 4(b)] the foil appeared relatively unchanged and remained intact with no evidence of damaging propagation of these fissures. It is worth pointing out, however, that the estimate of surface area for this foil (Table V) may be too low by a significant factor.

2.6 Impurity Analysis of Lithium Metal in the Hot Trap.

Residual lithium from the hot trap was analyzed for both cation and anion impurity content. Table VIII gives the concentrations of soluble and insoluble impurities found after aqueous dissolution. It should be noted that

a). Unexposed

10 μ m

b). Exposed: 538°C/216h
(Exit region of trap)

10 μ m

Figure 4 – Titanium foil surface characteristics (SEM).

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TABLE VIII
Analysis of Lithium Residue from the Hot Trap
Concentration (ppm)

Element	Soluble	Insoluble	Total
Zr	130	33000	33130+
Si	4900	150	5050
Ti	<50	3500	3500+
Fe	100	1700	1800
Na	1300	10	1300+
Ca	70	600	670
Cr	<50	550	550+
Mo	300	<50	300+
Mn	<50	150	150+
Ni	<50	150	150+
Al	30	40	70
Cu	<10	25	25+
F	159	-	159
Cl	165	-	165
Br	14	-	14
NO ₃	151	-	151
SO ₄	118	-	118

Note: Concentration (ppm) indicates micrograms of impurity found per gram of residual lithium metal dissolved - and does not represent actual concentrations in the liquid metal during operation.

these data do not reflect concentrations of the various elements in solution in the liquid metal, but simply the soluble and insoluble products of the aqueous reaction. In addition, this dissolution produced a lithium hydroxide solution with a pH greater than 10, which may well have promoted further chemical reactions.

3.0 THE COLD TRAP ECONOMIZER

3.1 Analysis of the Tube Surface

This economizer is 122cm long and is of the tube-and-shell type. Lithium flows from the main loop into the shell-side and to the cold trap, with return flow in the reverse direction down the central tube. Liquid metal temperature drops from 275°C to 200°C at the trap.

The cold trap is fabricated from 20 cm. dia. pipe and consists of an inner container packed with mesh into which the lithium flows before exiting at the bottom of the container to the outlet tube of the economizer. The trap essentially provides a large, low velocity, low temperature zone with a large metal surface area to promote precipitation of dissolved species. The basic features of the cold trap are illustrated in Figure 5.

Two sections were removed from the economizer tube so that the effects of lithium on the T304SS tube could be evaluated before and after passage through the trap. The tube sections were cut at 23cm. and 28cm. from the trap and, on a linear basis represent temperatures in the economizer of 214° and 217°C.

X-ray fluorescent analysis was performed on the two surfaces of the 1.6 cm. dia. tube samples. These data are given in Table IX below.

These results showed evidence of Ni and Fe deposition on the inlet side of the tube surface, while virtually no chemistry change was observed on the outlet surface. Scanning electron and optical microscopy, however, revealed considerable additional information, as shown in Figure 6. The inlet side of

Figure 5 – Schematic diagram of ELF cold trap.

TABLE IX
Surface Composition of T 304 SS Cold Trap Economizer Tube
(X-ray Analysis)

<u>Specimen</u>	<u>Temp (°C)</u>	<u>*Fe</u>	<u>Cr</u>	<u>Ni</u>	<u>Mn</u>	<u>Cu</u>	<u>Mo</u>
Unexposed	-	66.4	18.9	10.2	1.5	0.15	0.25
Inlet Side (23cm)	214	66.4	7.2	27.0	<0.1	0.22	0.17
Inlet Side (28cm)	217	74.0	5.4	17.4	<0.1	0.14	0.22
Outlet Side (23cm)	214	65.5	17.8	12.9	2.2	0.14	0.22
Outlet Side (28cm)	217	66.4	18.2	11.7	2.2	0.14	0.22

*Note: Data are given in weight percent.

the tube, at the 23cm location, was coated with a porous deposit approximately 12 μ m thick but the outlet side clearly indicated evidence of corrosion.

Although the typical equiaxed structure of micrograins, observed on ferritic surfaces in hot leg regions had not developed, what could well be an initial stage in the structural formation was present. The austenitic grain structure was clearly etched, as a result of its exposure during the 2000 hours of loop operation. The grain boundaries were grooved, micro-porosity was developing and the interior of each grain was attacked in such a way that it suggested grain orientation was influencing surface morphology development at this low temperature. It was indeed surprising that, with less than a 15°C temperature rise from the cold trap, the processes of corrosion were so evident.

Deposition of the lithium corrosion burden in the cold trap must have been very effective in order that solute contents of Fe and Ni in particular were reduced to a significant level below saturation at 215°C.

These observations indicate that cold trapping in a lithium system may be of limited benefit. If removal of hydrides, oxides, nitrides and carbides is of secondary importance (because the non-metallic elements in these compounds may be controlled by hot trapping) then removal of nickel and iron from the liquid metal to such an extent may be deleterious since the consequence is to increase the corrosion potential of the lithium.

a). Outer tube surface
Etch: 5% chromic acid.

20 μ m

b). Outer tube surface
(SEM)

5 μ m

c). Inner tube surface
Etch: 5% chromic acid.

20 μ m

d). Inner tube surface
(SEM)

5 μ m

Figure 6 — Surface features of the cold trap economizer tube.

3.2 Analysis of Lithium in the Economizer

It was not possible to separate lithium residues from the inlet side and outlet side of the economizer, but an analysis of the total residue at the 28cm location was performed. A comparison of these data, given in Table X, with results from residue analysis of lithium from the cold trap itself (given in Table XII) is indicative of the basic trends, but further studies are needed to determine what species remain in significant quantity in the lithium after passage through the trap.

There are many noteworthy items in Table X. The data - which reflect material suspended in the lithium in some form, not necessarily in solution - show high levels for Si and Cr compared with Fe and Ni. In addition, Mo is high compared with Zr and Ti, and is at the same level as found in the hot trap lithium residue. This fact is particularly interesting since it has been observed that Mo-bearing alloys such as T316SS and 2 1/4 Cr-1 Mo steel do lose Mo in the corrosion process.⁽²⁾

4.0 THE COLD TRAP

The cold trap was on-line continuously throughout the 2000 hours of loop operation. Flow varied between about 6×10^{-6} and 12×10^{-6} m³/s (0.1 and 0.2 gpm) and temperature for the majority of this period was held at 200°C $\pm 10^\circ$.

4.1 Trap Geometry

Details of the cold trap design are shown in Figure 5. Lithium flows into the trap from the shell side of the economizer, up the outside of the central mesh trap, contained in a 10cm dia. can, down through the mesh and back into the tube-side of the economizer.

4.2 Trap Analysis

The interior surfaces of the cold trap were found to be coated with deposit, similar to that observed on the inlet side of the economizer tube. Nickel

TABLE X

Analysis of Lithium Residue from the Cold Trap Economizer

Concentration (ppm)

Element	Soluble	Insoluble	Total
Si	5709	71	5780
Cr	1903	25	1928
Na	1695	1	1696
Mo	398	<10	398+
Fe	173	164	337
Al	242	1	243
Mn	121	10	131
Ca	87	2	89
Cu	55	1	56
Ni	<10	43	43+
Ti	<10	8	8+
Zr	<10	1	1+
F	135	-	135
Cl	92	-	92
Br	231	-	231
NO ⁻³	250	-	250
SO ⁻⁴	<1	-	<1

Note: Concentration (ppm) indicates micrograms of impurity found per gram of residual lithium metal dissolved - and does not represent actual concentrations in the liquid metal during operation.

content was again high, (30-40%). The T 304 SS cold trap mesh was also covered with corrosion products. Examples of these deposits are shown in Figure 7.

The cold trap mesh was analyzed for non-metallic impurities. Data for hydrogen, oxygen and nitrogen were obtained using high temperature extraction and gas mass spectrometry techniques. The results are given in Table XI. Assuming that diffusional effects are negligible for these gases at 200°C in this environment, the tendency for surface compound formation is greatest for oxygen - although the average value of 1317 ppm obtained for the 25 μ m dia. wire is still not very high. The values for hydrogen and nitrogen are much lower, suggesting that if these elements are bound up in compounds - the compounds are not adhering to or growing on the trap surfaces. Another possibility is that these compounds were removed during lithium dissolution.

TABLE XI
T 304 SS Cold Trap Mesh Non-Metallic Impurity Analysis

	Gas Content (ppm)		
	<u>Hydrogen</u>	<u>Oxygen</u>	<u>Nitrogen</u>
Unexposed	1.3	313	296
Inlet	15.4	1285	422
Middle	9.4	1645	226
Outlet	9.8	1020	175
Average for exposed mesh	11.5	1317	274

4.3 Impurity Analysis of Lithium Metal in the Cold Trap.

Residual lithium metal on the wire mesh was dissolved in water and analyzed in a similar manner to the residues from the hot trap. Data for soluble and insoluble species (in the hydroxide solution) are listed in Table XII.

a). Unexposed mesh

20 μ m

b). Exposed mesh

20 μ m

c). Exposed mesh

5 μ m

Figure 7 — Surface features of cold trap mesh. (SEM)

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TABLE XII

Analysis of Lithium Residue from the Cold Trap Mesh

Concentration (ppm)

Element	Soluble	Insoluble	Total
Ni	6938	26359	33297
Fe	1406	18451	19857
Si	10380	2987	13367
Cr	8650	4305	12955
Mn	2438	6853	9291
Ca	150	1054	1204
Na	938	<10	938+
Al	97	469	566
Cu	80	220	300
Mo	278	<10	278+
Zr	<10	123	123+
Ti	<10	57	57+
F	260	-	260
Cl	2114	-	2114
Br	140	-	140
NO ⁻³	573	-	573
SO ⁻⁴	1064	-	1064

Note: Concentration (ppm) indicates micrograms of impurity found per gram of residual lithium metal dissolved - and does not represent actual concentrations in the liquid metal during operation.

Nickel is, by almost a factor of two, the most prevalent element, followed by Fe, Si and Cr. Particulates containing these elements were retained in the trap but clearly were only loosely adhering to the trap surfaces.

5.0 CONCLUSIONS

Analysis of the hot trap and cold trap after operation in the Experimental Lithium Facility revealed many important chemical changes. These findings, although made following a limited period of loop operation, are valuable indicators for the design and operation of future ΔT lithium systems. The more important points are:

- o Titanium is preferable to zirconium as a nitrogen getter at 538°C because:
 - Titanium is an order of magnitude more efficient as a nitrogen getter than zirconium.
 - Zirconium suffers embrittlement as a result of exposure to lithium at 538°C. The reasons for this attack (e.g.: cold work in the foil, impurities in the lithium or a combination of these) are not yet identified. However, substantial quantities of Zr were found in the hot trap residues and on the titanium foil.
 - Zirconium demonstrated a greater affinity for nickel than titanium. This factor, coupled with the pickup of other metallic elements may be responsible for the inferior gettering properties demonstrated by this material.
- o When lithium is passed through a cold trap, the low velocity and high surface area conditions within the trap promote efficient deposition of the major metallic corroding species, (i.e., Ni, Fe, Si, Cr), and enhance the corrosion potential of the lithium to such a degree that it begins attacking the containment immediately after it leaves the

trap. If removal of hydrides, oxides, nitrides and carbides is of secondary importance (because the non-metallic elements in these compounds may be controlled by hot trapping) then removal of nickel and iron from the liquid metal to such an extent may be deleterious since the consequence is to increase the corrosion potential of the lithium.

6.0 ACKNOWLEDGEMENTS

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SECTION II

Hydrogen Isotope Monitoring in Lithium

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SECTION II
HYDROGEN ISOTOPE MONITORING IN LITHIUM

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"HYDROGEN ISOTOPE MONITORING IN LITHIUM"

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1.0 INTRODUCTION

A study of the dissolution behavior of hydrogen in lithium is of considerable relevance to all fusion reactor blanket technology, but particularly so to the inertial confinement concepts with their strong reliance on this liquid metal. Hydrogen isotopes, both bred tritium and unburned deuterium, will become dissolved in the lithium blanket and must be precisely monitored and extracted. Steam generator leaks may, depending on system design, cause ingress of hydrogen to the lithium circuit. Clearly, the prompt, on-line monitoring of these hydrogen solutes is important to both the efficiency and safety of the coolant/ breeder circuits of the reactor.

One of the major problems in studying the lithium-hydrogen system is the lack of a reliable analytical technique for determining low concentration levels (<1000 wppm) of dissolved hydrogen. Since lithium hydride is the only saline hydride which melts reversibly, very high temperatures are required in order to liberate the hydrogen for measurement. The usual method of heating the sample to 1000°C within an iron capsule and allowing the hydrogen to permeate out, results in uncertain data and a considerable base level value for the capsule blank.

For this reason the present work has concentrated on two alternative techniques for hydrogen determination in lithium. One, the development of a permeation-type hydrogen sensor, provides a continuous, on-line readout of dissolved hydrogen concentration, whereas the other method, equilibration with a metal foil, will be used for periodic checking of the sensor calibration. Experimental testing of the permeation meter and thermochemical calculations regarding the equilibrium technique were within the scope of the present contract.

2.0 TECHNICAL BACKGROUND

2.1 Lithium-Lithium Hydride Binary System

Of all the saline hydrides, lithium hydride has probably received more study than any other, and general surveys of the relevant literature have been published by Messer⁽¹⁾ and by Libowitz.⁽²⁾ With regard to monitoring solutions of hydrogen in liquid lithium, however, the most important data are the dissociation pressure isotherms and lithium hydride solubility at dilute concentrations, which have been published in more recent years. The isotherms above the monotectic temperature have been established by Veleckis⁽³⁾, Smith et al.⁽⁴⁾ and Shpil'rain⁽⁵⁾, and those below the monotectic by Katsuta⁽⁶⁾ and by Ihle and Wu.⁽⁷⁾ The hypoeutectic and hypereutectic liquid in the lithium-lithium hydride system have been reported by Hubberstey et al.⁽⁸⁾ and by Adams et al.⁽⁹⁾, respectively.

2.2 Hydrogen Monitoring Techniques

A number of different types of hydrogen sensor has been developed for use in liquid sodium. These are described and their applicability to lithium discussed.

2.2.1 Permeation Membrane Sensors

A convenient means of monitoring hydrogen levels in liquid sodium is based on the selective permeability of certain metals (notably nickel) towards hydrogen. Hydrogen which passes through a thin membrane of such a metal in contact with liquid sodium can be monitored by one of three techniques. Firstly, the permeating hydrogen can be removed by an inert sweep gas and measured with a gas chromatograph. Secondly, the partial hydrogen pressure associated with the liquid sodium can be allowed to equilibrate with a previously evacuated chamber on the other side of the membrane. This equilibrium pressure can then be measured with an ionization gauge or a mass spectrometer and related to hydrogen concentration using Sieverts Law. Thirdly, if such a vacuum chamber is continuously evacuated by a sputter ion pump, the pump current has been shown⁽¹⁰⁾ to be proportional to the hydrogen

flux across the membrane, and therefore to the hydrogen concentration. The first of these techniques is hampered by a long response time. The use of a mass spectrometer in the second method is probably more suited to the laboratory than in liquid sodium engineering loops. The dynamic mode using an ion pump, however, provides a rugged, accurate and continuous monitor of hydrogen levels, and can be conveniently checked or calibrated by a static method in which the equilibrium hydrogen pressure is measured by an ionization gauge. Meters based on this principle are routinely used on sodium test facilities and liquid metal cooled fast breeder reactors (LMFBR) in the U.S.A., Britain, France, Germany, Japan, and Russia as well as in other European countries. Of these, the French are the only workers who use a mass spectrometer rather than an ionization gauge for equilibrium measurements.

The leading commercially available meter is undoubtedly the Westinghouse design, Figure 1, which was developed at the Westinghouse Research and Development Center and the Advanced Reactors Division with the benefit of information liaison with the Argonne National Laboratory. The main advantages of this meter are its small size, rugged construction and proven ability in the concentration range 0.03-4 ppm hydrogen in sodium.

2.2.2 Electrochemical Cells

In 1968, Newcombe and Thompson⁽¹¹⁾ reported the use of an electrochemical cell for determining the solubility of hydrogen in liquid sodium. The cell can be described as:

Results were obtained in the temperature range 260° - 290°C, but above 300°C the glass electrolyte was attacked by liquid sodium. The mechanism of the cell was not fully understood, but it may be that an indirect reaction involving cations in the glass was involved.

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Figure 1 — Westinghouse liquid metal hydrogen meter.

A more promising electrochemical method, applicable at higher temperatures, was developed by Holden and Fuhrman⁽¹²⁻¹⁴⁾ at United Nuclear Corporation (UNC). Iron membranes, permeable to hydrogen, formed the cell electrodes and were connected through an electrolyte consisting of lithium chloride/potassium chloride eutectic containing 0.2-2.0 mol % lithium hydride, sodium hydride or calcium hydride. Their tests were expanded to include other electrolytes, the most suitable of which was found to be a 1.2 mol % solution of calcium oxide in lithium chloride/potassium chloride eutectic. This combination did respond to hydrogen concentration changes in both gas phase and liquid sodium tests, but the emf's generated were not in good agreement with theory. Indeed the mode of operation of such an electrolyte must have involved a more indirect reaction than with a simple hydride-containing salt.

No further reports of the UNC meter appeared in the literature, but the same basic design has been successfully taken up by Smith at the Central Electricity Generating Board (CEGB) Nuclear Laboratory in Berkeley, England. In 1972, he reported⁽¹⁵⁾ a cell similar to the UNC meter, with two iron membranes and a lithium chloride/potassium chloride eutectic electrolyte, Figure 2. Smith first repeated the experiment of Holden with lithium hydride and calcium hydride additions. He largely confirmed the earlier results, but with the aid of a theoretical interpretation of the dissociation pressures of various electrolyte mixtures, concluded that a solidified melt of calcium chloride/5% calcium hydride was more suitable. Initial gas phase tests of this electrolyte looked extremely promising, and it was also shown that a lithium/lithium hydride reference electrode was suitable for determining the low hydrogen concentrations in liquid sodium.

In 1974, the CEGB meter was made the subject of an invention disclosure in which the electrolyte was described as 10 mol % calcium hydride in calcium chloride. Apparently, such electrochemical hydrogen meters are now routinely used in the CEGB laboratory, and tests are underway to compare their performance with the more conventional diffusion type meters.⁽¹⁶⁾

Figure 2 – Central Electricity Generating Board hydrogen meter.

2.3 Hydrogen Isotope Extraction Techniques

Candidate hydrogen isotope extraction techniques for processing liquid lithium blankets have recently been reviewed by Buxbaum and Johnson.⁽¹⁷⁾ They conclude that at concentration levels in the parts per million range few separation processes offer any promise of success in recovering tritium from lithium under conditions permitting easy concentration and regeneration of the tritium in pure form.

Separation processes may be classified in ascending order of cost as mechanical separations, phase-change physical separations and finally chemical processes. Mechanical processes are not applicable because the tritium in lithium at typical blanket temperatures of 600°C is present as lithium tritide dissolved in the lithium, and hence is not recoverable either by filtration or by sedimentation.

Most of the phase-change separations are in principle applicable, but in practice are uneconomical. Simple cold trapping is not possible because the solubility of lithium tritide at the eutectic temperature for the lithium-lithium tritide system is too high.

Fractional distillation or indeed any vaporization process will not be practicable because an azeotrope exists for the lithium-lithium tritide system at excessively high concentrations for likely distillation temperatures. Watson⁽¹⁸⁾ has estimated that this azeotrope occurs at 0.05 atom ratio tritium to lithium at 1000°C. However, even in the absence of an azeotrope, or if the azeotrope were to form at sufficiently low concentrations, the vapor rates at the necessarily low pressures for distillation would lead to prohibitively large processing equipment. This factor also would preclude the use of solvent distillation (either azeotropic or extractive distillation) to break the azeotrope and effect the separation.

Liquid-liquid solvent extraction employing molten halide mixtures as solvent has been shown to be a practicable possibility by Maroni, Wolson, and Staahl.⁽¹⁹⁾ The distribution coefficient for lithium tritide between the salt melt and liquid lithium is around 2.0, and an electrolytic process for

recovering the tritium from the salt has been demonstrated by Calaway.⁽²⁰⁾ Unfortunately, although the equilibrium characteristics are favorable by normal standards, the very low concentrations dictate that the amounts of solvent be very large. Furthermore, the possibilities for contamination of the lithium by the salt are unattractive.

Other separation processes that have been suggested or studied for the recovery of tritium from lithium are permeation through metal membranes, absorption by liquid hydride formers,⁽²¹⁾ and absorption by solid hydride formers.

Although permeation rates can be high and permeation processes are used industrially to extract pure hydrogen from petroleum refinery gases, the use of permeation for tritium recovery from lithium in reactor blanket systems at low tritium concentrations does not appear to be practicable. Watson⁽¹⁸⁾ in his early and detailed appraisal of possible means of tritium recovery from fusion blanket systems concluded that permeation might be practicable provided sufficiently thin membranes of niobium coated with palladium on the low pressure side could be used. The purpose of the palladium was to forestall oxidation of the niobium, since low tritium pressures on the downstream was to be achieved by maintaining a low concentration of oxygen to promote water formation. Unfortunately, it is likely that inter-diffusion of the niobium and palladium would subvert their protective features over time. Furthermore, it is unlikely that nuclear construction standards would permit the use of thin enough membranes to avoid the need for very large scale equipment.

As early as 1954 Salmon⁽²²⁾ suggested the possibility of using a strong hydrogen getter like titanium or zirconium to extract tritium from lithium. However, these particular getters are at best marginal in competition with lithium. Much more attractive is yttrium, which has been studied in recent years for its application in fusion contexts by Hubberstey, Adams and Pulham⁽²³⁾ and Clinton and Watson.⁽²⁴⁾

3.0 EQUILIBRATION TECHNIQUE FOR HYDROGEN ANALYSIS

The most promising technique for off-line, intermittent analysis of liquid lithium for dissolved hydrogen content is probably the equilibration technique. Such a method is based on the selection of a suitable metal which does not react with lithium and into which hydrogen is favorably partitioned. If it is assumed that dilute solutions of hydrogen in lithium and in the metal obey Sieverts Law, that true equilibrium is established, and that no compounds are precipitated then the distribution coefficient, D_H , for the Li-M-H system is represented by:

$$D_H = \frac{C_{HM}}{C_{HLi}} = \frac{K_{HM}}{K_{HLi}}$$

where C_{HM} = Equilibrium concentration hydrogen in metal
 C_{HLi} = Equilibrium concentration hydrogen in lithium
 K_{HM} = Sieverts constant for hydrogen in metal
 K_{HLi} = Sieverts constant for hydrogen in lithium

Calculated temperature-dependent distribution coefficients for several refractory metal/lithium/hydrogen systems have been previously reported.⁽²⁵⁾ The group IV, V and VI elements Ti, Zr, V, Nb, Cr, and Mo all exhibited distribution coefficients less than 1 in the temperature range 500-1000°C. This means that in a ternary system hydrogen prefers to remain in lithium solution rather than become dissolved in the refractory metal, and these elements are therefore not suitable for an equilibration technique. Among the more stable metal hydrides, however, are those of the rare earth elements and particularly yttrium and scandium. Figure 3 shows the measured Sieverts constants for the yttrium-hydrogen⁽²⁶⁾ and lithium-hydrogen⁽²⁴⁾ binary systems as a function of temperature. Clearly, the former is the more stable solution and this is mirrored in the the calculated distribution coefficient for the Li-Y-H ternary system, also depicted in Figure 3. At the temperatures of interest, 400-600°C, the distribution coefficient is in the range 10^2 - 10^3 in favor of yttrium, and is therefore considered most suitable for an equilibration device. Experimental data⁽²⁷⁾ for the lithium/yttrium/tritium system are included with the calculated hydrogen values. No

Figure 3 — Temperature dependence of Sieverts Constant, K_s , for the Y-H and Li-H systems and the distribution coefficient, D_H , for the Y-Li-H system.

barriers to the establishment of true equilibrium are anticipated since the high solubility of hydrogen in yttrium (45 mol % at 500°C) should preclude the possibility of compound formation. Further experiments⁽²⁸⁾ on the gettering of hydrogen from lithium solutions have shown that the presence of heavy nitride layers on yttrium does not seriously impede the diffusion of hydrogen into the bulk of the metal, thereby upsetting the establishment of true equilibrium.

In conclusion, it appears that further work on the lithium-yttrium-hydrogen ternary system is fully justified in order to establish a reliable and reproducible analytical method for hydrogen determination in lithium. Such a technique would provide an invaluable means for periodically checking the calibration of on-line hydrogen meters.

4.0 EXPERIMENTAL

The lithium-hydrogen monitoring and processing test vessel is shown in Figure 4. It was constructed from Type 304 stainless steel and consisted of a reservoir of liquid lithium (~ 0.5 l) in which the hydrogen meters under test were immersed. A small (0.5 cm I.D.) side loop and miniature DC electromagnetic pump were welded to the vessel such that lithium could be continuously withdrawn from below the liquid surface and reinjected into the cover gas space of the reservoir. In this manner, if gettering was required, the lithium could be continuously circulated through a bed of the chosen material, or alternatively the side loop could be isolated by means of two bellows valves.

The two hydrogen meters tested in this program represented the two concepts which have proven most successful in liquid sodium systems, and which were described in Section 2.2, i.e., the diffusion-membrane and electrochemical types. The diffusion-membrane meter, Figure 1, was modified by the substitution of niobium for the nickel membrane, as described previously.⁽²⁹⁾ The electrochemical cell, Figure 2, was of essentially the same design as Smith's liquid sodium meter, and contained $\text{CaCl}_2/5$ wt % CaH_2 as electrolyte and a Li/LiH slurry as the reference electrode. A photograph of the two electrodes for this cell is shown in Figure 5.

Figure 4 – Lithium test vessel for monitoring hydrogen.

Figure 5 — The electrochemical hydrogen meter.

The liquid lithium reservoir was connected to a gas handling system which enabled the cover gas space to be evacuated and backfilled with either high purity argon or accurately known volumes of hydrogen.

5.0 RESULTS

When a new hydrogen meter is first operated, a thorough bakeout of the vacuum system is required before hydrogen permeation can be distinguished from outgassing. In this case, however, the niobium membrane meter could not achieve an ion pump signal less than 18 μA at a membrane temperature of 463°C. This was attributed to a significant initial concentration of hydrogen dissolved in the lithium. A level of, say, 1000 wppm would not be surprising since the lithium had not been purified by either filtration or gettering prior to filling the vessel. For the reasons described in Section 1.0, a straightforward chemical analysis of the lithium for hydrogen content could not be performed with any confidence. To check the hypothesis of residual hydrogen content, and to test the response of the meter, circulation of lithium through the gettering loop was initiated. The getter trap contained $\sim 500 \text{ cm}^2$ surface area of yttrium metal foil, and was operated at $\sim 460^\circ\text{C}$.

Figure 6 shows the change in hydrogen meter signal as a function of time during the gettering operation. Once flow was initiated, Point A in Figure 6, a steady decrease in meter signal, and hence dissolved hydrogen content, was observed. After only 4 hours, a 44% decrease in the original signal had occurred. At this time, Point B, the membrane and getter temperatures were raised to 481°C in order to make the meter signal more sensitive. This is achieved at higher temperatures by virtue of an increase in the permeability of niobium towards hydrogen and the temperature dependence of the Li-H Sieverts constant. Both of these temperature dependencies are manifest in Figure 6 by an increase in signal from Point B to Point C with no accompanying increase in hydrogen concentration. Gettering was then recommenced until a further 27.4% of the original hydrogen content had been removed (Point D) making a total of 72.6% removal in 21 hours. It should be noted that the calibration of hydrogen concentration per unit meter signal (μA) is not known at this stage and that the calibration along AB is different from that

Figure 6 — Response of hydrogen meter to gettering with Yttrium at 463 and 481°C.

along CD because of the temperature change. Approximate calculations based on membrane dimensions and niobium permeability indicate that the decrease in signal from A to B corresponds to at least 200 wppm hydrogen.

To monitor small changes in hydrogen concentration caused by additions of known volumes of hydrogen gas, it was found necessary to increase the membrane temperature to 510°C. Figure 7 shows the increases in ion pump current corresponding to additions of hydrogen to the lithium. The meter signal clearly changes linearly with hydrogen concentration at a rate of ~ 0.25 $\mu\text{A}/\text{wppm}$. The magnitude of this calibration, it must be stressed, is a function of both temperature and membrane dimensions. Since this calibration is at 510°C it cannot be used to provide a concentration axis for the initial gettering experiment depicted in Figure 6.

Further attempts at removing hydrogen from solution by circulation across the same getter sample were not successful. This can be rationalized by consideration of the amount of yttrium available for gettering. Since a large surface area of getter was considered desirable, the yttrium was used in the form of thin foil, resulting in an area of 500 cm^2 but a mass of only 8.8g. The calculated distribution coefficients for the Li-Y-H system (Section 3.0) were derived from a consideration of the Sieverts region of the Y-H system and indicated favorable gettering ability. From consideration of the Y-H phase diagram, however, once a hydrogen concentration of 0.4 mole fraction in yttrium has been reached then the non-stoichiometric hydride $\text{YH}_{1.8}$ begins to precipitate. At this point the system is no longer in the Sieverts regime but is in the plateau region, typical of metal hydrides, in which a constant partial pressure of hydrogen is associated with a wide range of compositions. In the Li-Y-H system at 500°C this means that the lowest achievable hydrogen concentration in lithium, when in contact with $\text{YH}_{1.8}$, is ~ 80 wppm. Gettering to a lower concentration can only be achieved by alpha phase yttrium, i.e., in the Sieverts region.

In our experiment, with only 8.8 g of yttrium, precipitation of $\text{YH}_{1.8}$ would have been achieved after approximately 230 wppm of hydrogen in lithium had been removed. Such a situation probably occurred after the initial clean up of residual hydrogen at the beginning of the experiment. In this manner, the

Figure 7 — Hydrogen meter response to lithium — hydrogen additions.

getter became effectively saturated. An alternative, although less likely, rationale for the failure to remove hydrogen later in the experiment, is that yttrium reacted with non-metallic solutes in the lithium and became blocked by the formation of an oxide, carbide or nitride surface layer. Either explanation, saturation or blocking, could have been tested by replacing the old getter with a sample of pure yttrium, but unfortunately time precluded this extension of the study.

Throughout the range of gettering and hydrogen addition experiments described above, no significant emf was measured in the electrochemical hydrogen meter which was simultaneously immersed in the lithium. Since valuable results were being generated by the permeation probe no attempt was made to remove and inspect the faulty cell while the lithium was at temperature. Such an inspection will be performed when the test vessel is decommissioned, if time and funding are available.

6.0 CONCLUSIONS

It has been demonstrated that the niobium membrane hydrogen meter can function in liquid lithium as a continuous monitor of hydrogen isotope build-up and removal at the concentration levels expected in the blanket of a fusion reactor. No conclusions regarding the applicability of an electrochemical cell type meter can be reached at this stage. The desirability of developing a new off-line analytical technique for hydrogen in lithium, in order to calibrate on-line meters, has been established. Calculations on the Li-Y-H ternary system have indicated that an yttrium equilibration technique should provide a reliable and accurate method for performing such analyses.

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SECTION III

Lithium Aerosol Formation in Relation to Fusion Reactors

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LITHIUM AEROSOL FORMATION IN RELATION TO FUSION REACTORS

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LITHIUM AEROSOL FORMATION IN RELATION TO FUSION REACTORS

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INTRODUCTION

This study of lithium aerosol formation constitutes part of an overall program^(1,2) at Westinghouse to develop the basic technology required for future large scale applications of liquid lithium. Liquid lithium has been proposed as the primary coolant and tritium fuel breeding medium for both magnetic and inertial confinement fusion devices. In the latter case, the large-scale use of lithium jets or streams as a shield to protect the reactor first wall from the damaging effects of the fusion microexplosion has also been proposed.⁽³⁾ A more immediate use of large quantities (9.1 m^3) of lithium will be in the Fusion Materials Irradiation Test (FMIT) facility presently under construction at the Westinghouse-Hanford site, in which a liquid lithium target will be bombarded with deuterons in order to produce high energy neutrons. This facility, scheduled for startup in the early 1980's, will provide a materials irradiation test environment which will approximate that expected in a fusion power reactor.

It is clear, therefore, that lithium will be present in a wide variety of environments, such as large coolant pools, tritium extraction equipment, laser reactor cavities, beam targets and divertors ranging from hard vacuum to pressurized, inert cover gases.

A basic study was initiated to examine the factors affecting the formation of lithium aerosols in various inert atmospheres, and to study the impact such aerosols will have on the use of lithium in fusion reactor technology.

AEROSOL FORMATION

The large-scale use of liquid sodium in fast breeder reactors and associated research and engineering loops has resulted in the repeated observation of sodium aerosol in inert cover gas spaces.⁽⁴⁾ This aerosol has also been referred to as sodium frost or mist and has been the source of considerable operational difficulties on several systems.⁽⁴⁾ Sodium transported in an aerosol form can interfere with the movement of sliding or rotating components, such as shafts or control-rod drive units, and can also provide a mechanism for transporting fission products and other impurities from the liquid sodium phase into remote spaces of the containment occupied by the cover gas. If a similar type of aerosol forms in the liquid lithium systems of a fusion reactor, similar potential problems will have to be considered. In addition, in a laser fusion reactor, it is possible that lithium aerosol particles within the fusion reaction cavity could attenuate or otherwise affect the power of the laser beam before it strikes the fuel pellet.

An aerosol can be defined as a system composed of solid or liquid particles dispersed in a gas, the particle size generally being in the range 10^{-2} to $10\text{ }\mu\text{m}$. It is important to distinguish between two different classes of aerosol, namely the dispersion type, which is formed by the atomization of a liquid, and the condensation type, which is formed when supersaturated vapors condense. Although the former type will certainly be of importance in the particular case of the lithium fast laser fusion reactor, it is the latter type which is of more general relevance and which is considered in this report. The generation mechanism of these condensation (or thermal) aerosols involves vaporization from a pool of molten lithium, quenching to a supersaturated condition by a cooler cover gas and subsequent agglomeration into larger particles. These particles will ultimately be removed by gravitational settling or by diffusive deposition on walls. These formation and removal processes proceed concurrently, eventually reaching a dynamic equilibrium exhibiting a constant aerosol concentration and particle size distribution.

This experimental study was directed towards the determination of the equilibration time and subsequent aerosol concentration as a function of pool temperature and cover gas pressure.

EXPERIMENTAL

Apparatus

A schematic of the aerosol generation and sampling chamber used in this work is shown in Figure 1. The chamber, which consisted of a glass bell jar with a stainless steel (A.I.S.I. Type 304) base flange, had a total internal volume of 47.3 liters. The system could be evacuated to $\sim 10^{-4}$ torr using a mechanical pump, oil diffusion pump and cold trap, or, alternatively, could be backfilled to ~ 650 torr with high purity helium or argon. Pressures within the chamber were measured by an absolute pressure gauge (Wallace-Tiernan 0-1030 torr), a thermocouple gauge (10^{-2} - 1 torr), or an ionization gauge (10^{-3} - 10^{-10} torr), depending upon the pressure range concerned. The base of the chamber incorporated a heated sump (8 cm diameter x 13 cm deep) containing liquid lithium. The lithium was supplied by an adjacent liquid metal test and purification loop which has been described in detail elsewhere.⁽¹⁾ The lithium contained, as major impurities (wppm), Na (383), K (70), and N (80). During normal operation of the system, a clean, lustrous liquid lithium surface (~ 50 cm²) was exposed within the test chamber. Provision was made, however, for this surface to be remotely covered with a stainless steel plate.

The base of the chamber was equipped with three circumferentially located ports at 0°, 90°, and 180°. These ports were equipped with either glass windows or a stainless steel aerosol sampling tube (0.5 cm I.D.) depending on the particular test being performed. The windows enabled a low-powered laser beam (2 mW He-Ne laser) to be directed across the lithium surface and viewed near the forward direction ($\sim 20^\circ$) or at a right angle (90°) to the beam travel. The aerosol sampling tube extended to a valved, disc filter holder through which known volumes of the chamber atmosphere could be drawn by means

Figure 1 — Lithium aerosol test system.

of a partial downstream vacuum. Typically, 0.1 μm pore size filters were used to trap the lithium aerosol, and the chamber gas was sampled at a rate of 0.5 liters/min.

Procedure

Each set of experimental data was collected in the following manner. The lithium temperature and cover gas pressure were set at the required values and the system was allowed to equilibrate for at least 2 1/2 hours. (The minimum time for the aerosol concentration to become constant; see later.)

First, a qualitative estimate* of the presence or absence of aerosol in the chamber was performed by visual observations at forward (20°) and right angle (90°) directions to the laser beam. Next, a quantitative determination of the aerosol concentration was made by withdrawing a known volume (~ 5 liters) of the cover gas through a filter which was subsequently removed and analyzed for lithium, sodium, and potassium by atomic absorption spectroscopy. For experiments at low cover gas pressures in which the chamber contained < 5 liters of gas, the lithium surface was covered and the chamber backfilled to a higher pressure where the normal sampling procedure could be employed. It was felt that the short duration of the sampling operation and the covering of the lithium surface greatly reduced the possibility of such low pressure samples being unrepresentative of the true aerosol concentration.

The results of these experiments are given in the next section as well as those of a number of aerosol equilibrations in which only the laser beam visibility test was performed.

RESULTS

Table I shows the aerosol concentrations (weight of alkali metal per unit volume of gas space) as a function of lithium pool temperature and cover gas

*The absolute sensitivity of this visual method was determined by separate experiments with smokes of known concentration.

TABLE I
AEROSOL CONCENTRATIONS OBTAINED BY FILTRATION TECHNIQUE

Lithium Pool	Cover Gas	Aerosol Concentrations ¹ (μg/l)	
Temp. (°C)	Pressure (torr)	Lithium	Sodium
	<u>Argon</u>		
24	460	0.05	0.00
327	570	<0.04	0.33
371	540	0.05	0.23
374	32	1.37	0.10
427	0.3	0.13	0.00
427	33	0.32	0.19
427	577	0.72	0.63
430	0.03	0.20	0.00
430	5	0.19	0.09
477	538	6.16	3.91
482	585	6.05	3.79
482	438	6.78	3.02
482	27	4.41	0.58
482	3	1.59	0.66
482	0.3	1.33	0.07
482	0.03	2.24	0.11
510	0.03	2.94	0.72
	<u>Helium</u>		
482	469	1.45	0.55
482	35	0.11	0.52
484	5	0.02	0.26
480	0.3	0.05	0.51
482	0.03	0.14	0.25

1. Corrected for blank concentrations.

9172A-845A(S1765)

pressure. Seventeen different conditions were sampled with argon cover gas and five with helium. The aerosol concentrations are corrected for typical blank filter values; these were negligible for lithium, but were significant for sodium. Even after this correction, it was noted that under some conditions a considerable quantity of sodium was present in the aerosol. Sodium was a major impurity in the liquid lithium pool, and the mechanism by which it contributes to aerosol formation is discussed below. The other alkali metal impurity, potassium, was not found on the filters in any measurable quantity.

Each set of temperature/pressure conditions was equilibrated for a minimum of 2 1/2 - 3 hours before measurements were taken. The necessity for this is demonstrated in Figure 2, which depicts the aerosol concentration as a function of time at 482°C and 550 torr argon. This curve is typical of the rate of formation of aerosol in the particular chamber used for this experiment, and shows that the processes of aerosol coagulation and settling required at least 2 1/2 hours to equilibrate.

The observations concerning laser beam scattering as a function of lithium temperature and cover gas pressure are summarized in Figure 3 (a) and (b) for argon and helium respectively. The results are reported as simply "visible" or "not visible," and no attempt was made to measure the extent of scattering, although an estimate of this is derived in the next section. Both 90° and 20° scattering was observed at high aerosol concentrations, but only 20° scattering at the lower concentrations. The decision regarding visibility was based on the 20°, or forward, scattering.

DISCUSSION

Laser Beam Extinction and Scattering

Aerosol particles are efficient interceptors of light by means of reflection, absorption, and diffraction.*⁽⁵⁾ In laser fusion applications, one is

*Refraction does not occur because alkali metal particles are opaque.

Curve 721440-A

Figure 2 – Kinetics of aerosol formation.

Figure 3 – Temperature/pressure regimes for laser scattering detection of lithium aerosol.

concerned with the combined loss of beam intensity by all three mechanisms. A convenient measure of this loss is the extinction coefficient, b , defined as the fractional loss in beam intensity per unit pathlength. In symbols

$$b = \frac{\Delta I/I}{\Delta X},$$

where I is the beam intensity, and ΔI is the intensity loss over a distance ΔX . A convenient set of units for b in the discussion here is percentage loss/meter ($b \times 100$).

Two laser beam scattering techniques were considered for the detection of lithium aerosol in the chamber. The first method would measure the loss in intensity of the laser beam directly with a silicon cell photometer. The major defect in this technique, however, is its lack of sensitivity, since, for small extinction values ($b \sim 1\%$ /meter), the difference between the two intensities, ΔI , is small and tends toward large error. The second method, employing the qualitative visual detection of scattered light, is far more sensitive and was, therefore, employed in this study. Quantitative tests with dilute smoke established that the lower limit of beam visibility corresponded to an extinction coefficient of 0.01% /meter.

Extinction per unit mass of aerosol depends strongly on the size of the aerosol particles.⁽⁵⁻⁷⁾ The highest extinction values occur for particle diameters near $d_m = \gamma/\pi$, which, for a He-Ne laser, gives $d_m = 0.2 \mu\text{m}$. Above this diameter, the extinction decreases because larger particles have less

cross-sectional area per unit mass; below this diameter it decreases because the scattering mechanism changes to one with sharply decreasing efficiency (Rayleigh scattering, $d \ll \gamma$).

This optimum aerosol size for laser beam extinction, $0.2 \mu\text{m}$, lies approximately in the middle of the expected range of particle sizes for this experiment. It has been shown, for similar sodium systems,⁽⁸⁾ that particles $< 0.01 \mu\text{m}$ tend to grow by coagulation while those $> 10 \mu\text{m}$ are most susceptible to removal by gravitational setting.

Assuming a lower limit for visual beam detection of $b=0.01\%/meter$, and a typical particle size of $0.2\ \mu m$, the lowest aerosol mass concentration that should be detectable in this experiment is $0.36\ \mu g/liter$. Theoretically, then, one would expect the diagonal dividing lines in Figures 3 (a) and (b) to roughly correspond with this concentration.

In summary, the laser beam scattering experiments indicate that, qualitatively, more lithium aerosol is formed at higher temperatures and higher cover gas pressures for both argon and helium. Quantitatively, the temperature/pressure regime corresponding to an aerosol concentration of $\sim 0.36\ \mu g/liter$ has been defined. This limit occurs at higher temperatures and pressures for helium than for argon.

Aerosol Concentrations - Filtration Experiments

A more precise description of aerosol behavior as a function of both lithium temperature and cover gas pressure is obtained from the filtration data. These two dependencies can be separated by plotting aerosol concentration isobars (Figure 4) and isotherms (Figures 5 and 6).

The first of these plots clearly shows that over the argon pressure range covered, 0.03 - 550 torr, there is negligible aerosol below $\sim 400^\circ C$. At temperatures $>400^\circ C$ the aerosol concentration rises steeply, with the strongest effect occurring at the higher cover gas pressure. This temperature dependence is clearly related to the vapor pressure of the lithium which is included on the axis in Figure 4 and is also in excellent agreement with the laser scattering results of Figure 3 (a).

The dependence of lithium aerosol concentration on cover gas pressure is shown in Figure 5. With argon as the cover gas, pressures in excess of 1-10 torr at $482^\circ C$ and 10 - 100 torr at $427^\circ C$ are required before appreciable aerosol is formed. Again, this is in close agreement with the qualitative predictions of Figure 3 (a). The lowest argon pressure (0.03 torr) data point at $482^\circ C$ is thought to be anomalously high, possibly due to the backfilling procedure required for filter sampling at such low pressures.

Figure 4 — Argon cover gas isobars.

Curve 721438-A

Figure 5 — Lithium aerosol isotherms.

Curve 721437-A

Figure 6 — Sodium impurity aerosol isotherms (over liquid lithium).

The pressure dependence with helium as the cover gas, Figure 5, shows that, at 482°C, not only is the aerosol concentration less than in argon, but that an order of magnitude higher pressure is required before a measurable aerosol is formed.

To summarize, lithium aerosol is formed in increasing concentrations as the pool temperature and/or cover gas pressure are raised. Less aerosol is formed with helium than with argon under a given set of conditions. These findings can be rationalized as follows:

Near the surface of the lithium pool a boundary layer of cover gas is present in which two processes occur simultaneously, lithium diffusion and coagulation to form aerosol particles, and sedimentation of larger particles back into the lithium pool. In the bulk of the chamber, turbulent thermal convection currents exist by virtue of the large temperature difference between the lithium pool and the chamber walls. These provide constant mixing for those aerosol particles which are successful in penetrating the boundary layer at the lithium pool surface. Changing either to a lighter cover gas, such as helium, or to a lower cover gas pressure tends to increase coagulation and sedimentation rates in the boundary layer and hence will lead to a lower aerosol content in the bulk of the system. Increasing the lithium pool temperature increases the vapor pressure at the lithium surface. It is hypothesized that this produces a higher flux of aerosol particles diffusing through the boundary layer, thus increasing the aerosol concentration in the bulk of the system. This dependence of aerosol concentration on vapor pressure might be expected to result in impurity species with higher vapor pressures than lithium also being present in the aerosol. Sodium, which is several orders of magnitude more volatile than lithium, is an ever-present impurity in lithium, and was present at a level of ~380 wppm in these experiments. Evidence of a significant percentage of sodium in the lithium aerosol is clear from Figure 6 which indicates that at 482°C, with an argon cover gas, as much as 36% of the aerosol can be sodium.

Comparison with Previous Work

There have been no previous reports of aerosol formation in lithium/inert gas systems. Isolated studies have been made on analagous sodium systems, however, notably at Argonne National Laboratory⁽⁹⁻¹²⁾ where the work was confined to flowing inert gas systems operating at atmospheric pressure. It was reported⁽⁹⁾ that sodium vapor formed aerosol within a few millimeters of the pool surface if the cover gas was at least 50°C cooler than the sodium. Interestingly, less aerosol was formed with helium as the cover gas than with argon⁽¹¹⁾ under otherwise identical conditions, just as in the present experiments. This general finding has been further confirmed by experiences at the French liquid sodium cooled breeder reactor, Rapsodie.⁽¹³⁾ Considerable early problems caused by sodium aerosol have been largely eased by switching from argon cover gas to helium.

Aerosol filtration studies at Argonne⁽¹⁰⁻¹²⁾ indicated that sodium aerosol concentrations at 400°C were a factor of nine greater than those expected simply from vapor pressure. This phenomenon was ascribed to the presence of convective recirculation between the colder cover gas and the molten sodium pool. More recent Japanese work⁽¹⁴⁾ found a sodium aerosol concentration varying between 3 and 10 times greater than the vapor concentration at temperatures in the range 320° - 520°C.

In the present work, lithium aerosol concentrations at 482°C were a factor of ten greater than the vapor concentration with an argon cover gas, but only a factor of two with helium. The sodium impurity level in the aerosol was a factor of 4 greater than the equilibrium vapor concentration estimated by applying Raoult's Law.

These multiplying factors for comparing aerosol-phase concentrations with predicted vapor concentrations are, of course, very much dependent on the experimental system being used. The greater the degree of quenching and/or convection possible in the cover gas space, the higher will be the aerosol concentration. Nevertheless, it is apparent from the present lithium data,

and from the sodium results in the literature that, under quench conditions, the alkali metal concentration in the cover gas can be greater than the vapor pressure prediction by a factor as high as 10.

Conclusions Relevant to Fusion Reactors

The close relationship between aerosol concentration and vapor pressure dictates that problems due to deposition that have been encountered in sodium systems should be far less severe in a lithium-cooled reactor. Nevertheless, the system can be further optimized by the selection of helium as the cover gas rather than argon. With regard to the specific topic of laser fusion reactors, there appears to be little possibility of a thermally generated aerosol becoming sufficiently dense to attenuate the driver beam. This statement refers to aerosol derived from the lithium wall at its average temperature. However, it is expected that, following each laser fusion explosion, a large lithium vapor pressure transient will exist momentarily. If supersaturated, this vapor could coagulate very rapidly to form an optically dense cloud of particles which ultimately would be removed by gravitational settling. This type of transient aerosol formation lies beyond the scope of the present work.

At proposed nominal laser fusion reactor chamber conditions of 0.03 torr and 510°C, the lithium aerosol concentration reaches a maximum of only ~ 3 $\mu\text{g/liters}$ after a full 3 hours equilibration. A serious reduction in laser beam intensity ($b = 1\%/meter$) would require ~ 36 $\mu\text{g/liters}$. The situation becomes even more favorable if the 0.03 torr partial pressure is composed of helium rather than argon.

One aspect of this work, which might have more serious repercussions for reactor design, is the finding that relatively low concentrations of sodium impurity in the lithium can become concentrated in the cover gas phase as aerosol. Not only could this lead to a possible deposition problem but, in a working reactor, the sodium will become activated to produce Na^{24} isotope which is a 8-emitter with a half-life of 14.9 hours. The maximum permitted sodium impurity level will therefore be an important factor when considering the radiation level, even in remote parts of the lithium loop system.

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Appendix (Published Paper)

Materials Behavior in Lithium Systems for Fusion Reactor Applications

MATERIALS BEHAVIOR IN LITHIUM SYSTEMS FOR FUSION REACTOR APPLICATIONS

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The corrosion behavior of austenitic and ferritic steels in flowing 538°C (1000°F) lithium is presented as weight loss vs. time data. The measured weight losses are shown to be due to loss of alloying elements from the near surface regions. Corrosion rates of the austenitic alloys are from 3 to 5 times greater than the ferritic alloys examined, but both alloy types exhibit a "downstream effect".

1. INTRODUCTION

Several inertial confinement fusion (ICF) concepts utilize a liquid lithium blanket for protection of the reactor first wall from the damaging effects of the fusion reaction, to breed tritium, to convert the fusion energy into thermal energy, and as the heat transport medium. [1] Temperatures up to 538°C (1000°F) are envisaged for lithium in contact with both coolant piping and the first wall. Much of the information available in the literature on materials compatibility in lithium was generated in non-flowing systems at temperatures in the range 705-926°C (1300-1700°F) and is therefore difficult to apply to reactor concepts employing high flow rate systems at 538°C. [2] Therefore, in order to provide design data for necessary safety and reliability requirements in the areas of long term corrosion and mechanical property effects, an experimental program was initiated, in which candidate containment materials, both austenitic stainless steels and the ferritic steels, were exposed to flowing lithium for an extended period of time. In this paper, the preliminary corrosion behavior of these materials is compared. The effects of different heat treatments on corrosion behavior of the ferritic alloys and the mode of attack by the lithium, as observed in a subsequent metallographic examination are described. The performance of specimens of dissimilar metal weldments in lithium is also discussed.

2. EXPERIMENTAL TECHNIQUES

The Experimental Lithium Facility (ELF), a unique Westinghouse-owned system for fusion materials and systems studies, was used to obtain the corrosion data presented in this paper. This system, shown schematically in Figure 1, is an all austenitic stainless steel loop which was operated with a hot leg sample section temperature of 538°C (1000°F), and a ΔT of 152°C (275°F). The main loop is of all welded construction

Figure 1. Schematic of the Experimental Lithium Facility (ELF)

and uses 25mm (1 in.) O.D. x 1.65mm (0.065 in.) wall Type 304 stainless steel tubing. The total lithium inventory is 13.6 kg (30 lb). Test samples are located in the hot leg and cold leg test sections and may be periodically removed to give the time dependency of the mass transfer rates.

The lithium flows from the electromagnetic pump progressively through the flowmeter, the shell side of the cold leg economizer (heat exchanger), a heater section, an isothermal hot leg test section, the tube side of the economizer and a finned tube heat exchanger. The ELF system also includes four separate sub-loops or bypass lines, which function as cold trap and hot trap systems, and impurity monitoring and flow-through sampler stations. These sub-loops constructed of 12.7mm (0.500 in.) O.D. x 1.65mm (0.065 in.) wall 304 stainless steel tubing are used to monitor and control the lithium impurity content.

A glove box may be located over either the hot or the cold leg of the system and enables withdrawal of samples to be performed while

loop operation continues. The argon atmosphere purity is maintained by means of a self-contained dry train. Tubular specimens 12.7mm (0.5 in.) long x 20.3mm (0.800 in.) diameter were exposed to lithium on the outside surface, with the flowrate in the annulus between the containment and sample tubes being $7.2 \times 10^{-8} \text{ m}^3/\text{s}$ (1.65 gpm). The lithium velocity in the hot leg test section was 1.82 m/s (6 fps).

Materials chemistry and heat treatments are shown in Table 1. Samples were periodically removed from the ELF for evaluation. Prior to weighing, they were cleaned in water and dried. Microstructural changes resulting from lithium corrosion were evaluated by optical and scanning electron metallography and surface chemistry changes by energy dispersive x-ray analysis.

Table 1 Materials and Heat Treatments

Material*	Heat Analysis (wt. %)						
	Fe	Cr	Ni	Mo	Mn	Si	C
304 SS	71.1	18.64	8.1	--	1.79	.31	.063
304L SS	69.3	18.5	10.3	--	1.27	.61	.026
316 SS	67.3	16.78	11.6	2.39	1.56	.33	.045
2½Cr-1 Mo**	95.8	2.35	--	1.02	0.53	.22	.12
9Cr-1 Mo**	89.9	8.08	--	0.96	0.45	.53	.11

*All materials were tested in as received, annealed condition.

**These alloys were also tested after the following heat treatments:

HT#1: 1h @ 925°C (1700°F) in vacuum; cool @ 45°C (83°F) per hour to 704°C (1300°F), hold for 2h then furnace cool in vacuum to room temperature.

HT#2: Repeat HT#1, and follow with 8h @ 775°C (1427°F) for 8h; cool in vacuum to room temperature.

The lithium, originally purchased from Foote Mineral Company in ingot-form (99.98% nominal purity), was found to contain 0.027 weight % sodium as the major impurity.

3. RESULTS AND DISCUSSION

3.1 Corrosion Data

The corrosion behavior of both austenitic and ferritic alloys is illustrated in Figure 2. These weight loss data, which are taken only from the samples at the entrance to the test section, exhibit a linear dependence on exposure time in lithium for the austenitic alloys. The 304 stainless steel has lost 10% more weight than the 316 alloy, which may be a result of the lower alloying content of the

Figure 2. Weight Loss of Austenitic and Ferritic Materials as a Function of Exposure Time in Flowing Lithium at 538°C (1000°F)

former, or the presence of molybdenum in the 316. Data for the ferritic materials show more scatter, but it is evident that these alloys exhibit improved short-term corrosion behavior, with weight losses at 948 h being of the order of three times lower than the 300 series stainless steels. There are indications from a plot of weight loss vs. (time)^{1/2} that the corrosion rate of the austenitic alloys may exhibit a parabolic dependence on time of exposure. However, longer term data are required before the rate dependence can be classified. No similar statement can be made with respect to the ferritic alloys, but it is clear that for both the 2½Cr-1 Mo and the 9Cr-1 Mo alloys, heat treatment #1, which was designed to produce a uniformly dispersed carbide phase in the matrix, with the minimum amount of Fe₃C phase results in a 20% lower weight loss than as received material. An evaluation of the merits of heat treatment #2 must await the availability of longer term data. The 9Cr-1 Mo alloy tends to show the lowest corrosion rates of all the materials tested within the limits of this experiment.

Another important facet of this corrosion study is the evidence of a downstream effect on corrosion rate, as shown in Table 2. Both

Table 2 Effect of Downstream Location (L/D)* on the Corrosion Rate at 538°C (1000°F) of Austenitic and Ferritic Materials After 948 h Exposure to Flowing Lithium

Material	Corrosion Rate at Indicated Downstream Location 10^{-6} g/m ² ·s (mpy)**			
Austenitics	L/D		L/D	
304 SS	84	9.28 (1.46)	147	7.35 (1.15)
304L SS	91	7.99 (1.25)	154	7.38 (1.16)
316 SS	98	7.63 (1.20)	160	7.46 (1.17)
Ferritics				
2½ Cr-1 Mo	105	3.01 (0.48)	168	2.32 (0.37)
2½ Cr-1 Mo HT #1	112	2.45 (0.39)	175	1.21 (0.19)
2½ Cr-1 Mo HT #2	119	2.43 (0.38)	182	1.69 (0.27)
9 Cr-1 Mo	126	2.74 (0.44)	189	1.85 (0.30)
9 Cr-1 Mo HT #1	133	2.21 (0.35)	196	1.67 (0.27)
9 Cr-1 Mo HT #2	140	2.91 (0.47)	203	2.06 (0.33)

*Where L is the distance from heater exit to sample and D is the hydraulic diameter of the pipe/tube.

**mpy - an engineering term used to denote mils (10^{-3} in.) of thickness loss per year.

classes of materials exhibit a reduction in corrosion rate the further away they are located from the exit of the heater; e.g. Type 304 shows a reduction in rate from 9.28×10^{-6} (1.46) to 7.35×10^{-6} (1.15) g/m²·s (mpy) over a distance of 152mm (6 in.) or 63 L/D's in the isothermal hot leg test section. This effect, noted in studies with similar sodium systems, [3] results from the fact that the liquid metal becomes more saturated with alloying elements removed from the specimen surfaces as it flows through the test section. As a consequence, its corrosion potential is reduced with respect to L/D position. The observed corrosion rates for all materials tested are more than an order of magnitude greater than results from equivalent sodium compatibility studies, which is indicative of the more aggressive lithium environment.

3.2 Microstructural Data

The weight losses are accompanied by changes in the near surface microstructure of the materials, as shown in Figure 3. Prior to

exposure, the microstructure of the 300 series stainless steel samples consisted of equiaxed grains (ASTM #7 and 8). The ferritic alloys exhibited microstructures with an ASTM #8 and 9 grain size, consisting of ferrite with some pearlite, bainite and finely distributed carbide particles. The surface region of each alloy showed signs of residual cold-work and slip line formation resulting from the final machining to size operation. The Type 304 stainless steel sample near surface region changed to a fine grain, ferritic structure as a result of the lithium exposure, as did the low carbon Type 304L (not shown). This change, evident even after 210 h -- the first time the samples were removed from the ELF system, clearly indicates a rapid phenomenon with a short incubation time. Similar surface changes to those shown in Figure 3, were observed in samples of the ferritic alloys in the as received and in the HT #1 conditions, suggesting that heat treatment at this stage in the corrosion process has not had a major effect on corrosion rate. A scanning electron microscopical examination coupled with surface x-ray analysis has confirmed that a surface change has taken place. All materials tested exhibited a surface appearance, resembling that shown in Figure 4: very fine iron rich grains with evidence of grain boundary grooving. The austenitic alloys have lost significant percentages of their original surface chromium and nickel contents with a resultant relative increase being observed in iron. The 2½ Cr-1 Mo alloy surface chemistry exhibited increased levels in most elements except iron, (See Table 3). All alloys after lithium exposure indicated surface iron contents in the 83-89%, which is consistent with the ferritic layer observations.

Samples of dissimilar metal welds (2½ Cr-1 Mo/304 and 9 Cr-1 Mo/304) were found to exhibit no unusual surface features after exposure to lithium for 948 h. The only deleterious effects were a result of the thermal exposure and consisted of internal cracking in the heat affected zone of the 2½ Cr-1 Mo/304 welds. Since no post heat treatment was performed on any of these welds, this observation was not unexpected.

3.3 Analytical Chemistry Data

The ELF system operational history, shown in Figure 5 together with the analytical data can be used to evaluate the efficiency of the hot and cold trap sub loops. The cold trap operated continuously at 210°C (400°F) with ~5% of the main flow passing through the trap, but the hot trap, containing both zirconium and titanium foil, was only operated for three 72-hour periods at 538°C (1000°F). Data from flow-through samples indicate that the oxygen analyses (by mercury amalgamation) decreased from 608 to 112 ppm, and the nitrogen analyses (by micro Kjeldahl)

Figure 3. Cross Sectional Micrographs of Candidate Materials After Exposure to 538°C (1000°F), Flowing Lithium for 948 h. (Etchant : a) and b) Glycerol/HCl/HNO₃, c) 4% Nital and d) 8% Nital)

Figure 4. Surface of 2 1/4 Cr - 1 Mo Alloy (HT #2) After 948 h in 538°C (1000°F), Flowing Lithium.

were maintained in the range 70–100 ppm. One ELF sample was analyzed at Argonne National Laboratory (courtesy V. Maroni) and the result, 72 ppm, confirmed the 77 ppm nitrogen measured in this laboratory; a value of <1 ppm carbon was also determined on the same sample.

This level of nitrogen is lower than obtained in other lithium studies, [4,5] and is considerably lower than the solubility at the cold trap temperature (1620 ppm). It appears, therefore, that the three relatively short periods of gettering have significantly reduced the nitrogen concentration, although not to the thermodynamically predicted level (<1 ppm @ 538°C). Lower values might, therefore, be attainable by increasing the duration and/or the temperature of the gettering. A level of <100 ppm, however, if it can be maintained over long periods, is certainly satisfactory and should allow the corrosion data to be meaningful and reproducible.

Table 3 Surface Analysis Changes Resulting From Exposure to 538°C (1000°F) Lithium

Material	Exp. Time (h)	Surface Analysis (wt. percent)					
		Fe	Cr	Ni	Mn	Si	Mo
304 SS	0	70.0	19.3	6.1	2.3	1.3	0.9
	948	84.1	8.9	2.9	1.9	2.1	0.17
304L SS	0	71.0	18.1	8.8	0.9	0.9	0.25
	948	85.3	9.4	2.4	1.7	1.1	0.13
316 SS	0	69.3	16.8	10.4	1.2	1.2	2.3
	948	82.9	10.4	3.0	2.1	0.7	1.0
2½ Cr-1 Mo HT #2	0	96.5	2.2	1.6	0.1	0.7	0.4
	948	88.8	5.6	2.0	2.0	1.4	0.2

These analyses are semi quantitative values obtained from an SEM/EDAX system and may be used to indicate trends in surface chemistry.

Figure 5. Loop Operating and Analytical Chemistry History of ELF System

4. SUMMARY AND CONCLUSIONS

In 538°C (1000°F) flowing lithium, austenitic and ferritic steels lose weight, with the region near to the exposed surface exhibiting a ferritic layer. The weight loss at 948 h for the ferritic alloys is a factor of three less than that for the austenitic alloys. However, caution should be exercised here, because the loop tubing is austenitic

and dissimilar metal transfer between this tubing and the ferritic samples is possible, such that the apparent weight loss of the ferritic steels would be less than in the absence of such transfer. Therefore, the relative difference in weight loss between the austenitic and ferritic materials may in this case be enhanced. Additionally, steady state corrosion may not have been reached for the austenitic steels. The weight loss of the 300 series steels results from the removal of alloying elements by the lithium, but weight loss of the ferritic alloys appears to be due to iron removal. Type 316 stainless steel exhibited the lowest weight loss for the austenitics. All alloys exhibited a corrosion rate affected by downstream location with respect to the heater exit. Within the limits of this experiment, it is noted that no deleterious effects were noted on dissimilar metal welds exposed to lithium, and that hot trapping and cold trapping can be used to maintain the lithium chemistry in the range 70-100 ppm nitrogen and ≤ 110 ppm oxygen. These data are from an on-going program, from which longer term information will be obtained in the areas of corrosion and materials behavior in flowing lithium.

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