

**Project Title: Fundamental and applied experimental investigations of corrosion of steel by LBE under controlled conditions: kinetics, chemistry, morphology, and surface preparation.**

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**Abstract:**

An innovative research program is proposed to investigate the corrosion of steel by lead alloys, and in particular lead-bismuth eutectic (LBE). In our previous work, some steels were found to be far more resistant to corrosion by LBE than others depending on surface preparation (cold working). This program would allow testing of crucial hypotheses about the causes of the observed increased corrosion resistance. We propose to build a new test facility at UNLV to expose steel samples to LBE as well as facilities to prepare steel samples as indicated by our work.

The unique capabilities of the test system will make investigations of the fundamentals of lead alloy corrosion under a variety of conditions feasible and lead to the establishment of new protocols for the minimization of molten lead alloy corrosion of structural materials. These capabilities include fast and controlled sample introduction via a vacuum load lock system, both high temperature operation and controlled chemical environment by the use of alumina and silica or other refractory materials for lead alloy containment, and highly modifiable flow systems for determination of fundamental kinetics and parameters and thus accurate modeling of lead alloy systems.

In parallel with the test effort we will prepare well characterized samples of candidate materials and model systems. In particular we shall look at modifications of the sample surface and near surface composition (e.g. the effects of cold working). In addition we shall investigate the feasibility of using the mass selected ion facility at UNLV (Mitchell, Conklin and Farley 2003) developed by Prof. Farley to both modify surface composition (e.g. ion implant oxygen to compensate for oxygen deficiencies) of test samples and to introduce stable isotope labels into known steels to determine mass transport properties inside the steels.

**Scientific Background:**

The Transmutation Research Program (TRP) at UNLV is part of the Advanced Fuel Cycle Initiative (AFCI) within the Advanced Nuclear Research Office (NE-20) at DOE. The plans for transmutation of nuclear waste involve the use of reactors or accelerators to transmute spent nuclear fuel, reducing the volume and radiotoxicity of the waste. The transmutation process places stringent requirements on the materials to be used: materials must be capable of withstanding very high particle fluxes, elevated temperatures, and chemical corrosion. Materials must be found for a coolant that can conduct away the high heat load. Materials questions are critical to the feasibility of the entire transmutation project.

Lead Bismuth Eutectic (LBE) is of interest as both a coolant and a spallation target in proposed transmutation schemes for radioactive waste. Unfortunately, hot LBE corrodes most engineering materials. An absolutely critical issue is corrosion in the LBE/stainless steel system. The 1999 *Roadmap for Developing Accelerator Transmutation of Waste (ATW) Technology* lists "Coolant Chemistry and Materials Compatibility" under the Target/Blanket R&D Activities.

There have been previous studies of LBE, especially by the Russians, who have over 80 reactor-years' experience with LBE coolant in their Alpha-class submarine reactors. The Russians found that the presence of small amounts (ppb) of oxygen in the LBE significantly reduced corrosion. The suppression of corrosion is believed to arise from the formation of a protective oxide layer on the metal surface. The oxide layer passivates the surface, retarding the corrosion rate. In principle, such an oxide layer can be self-healing, because if the oxide layer is disrupted for any reason, a fresh oxide layer would re-form. *However, a fundamental understanding and verification of oxygen's role is still incomplete*

In the present grant period, we studied a series of nuclear grade low carbon 316 stainless steels that varied only by their surface preparations. Our investigation was driven by a study of number of steels tested at IPPE in Russia under contract to LANL. Two classes of samples were found – resistant steels (the cold worked samples) and non-resistant steels (annealed and etched samples). The cold rolled 316 sample showed an order of magnitude lower corrosion at long times (3000 hr) at high (550 C) temperature than all of the other samples under test at the same time.

The reasons for this difference were investigated (Johnson et al., J. Nucl. Mat. 2004). Imaging the oxide layers of the 316 samples showed a fairly uniform 10µm thick oxide layer in the annealed 316 samples and a ~1 µm thick oxide in the cold-rolled 316 samples. We also observed that the LBE was confined to the surface of the oxide; there was little or no penetration of the coolant into the protective oxide layer.

We found two forms of oxide layer (figure 1). On annealed 316 and the other alloys we found a “complex” structure, with a surface composed primarily of iron oxide and an underlying oxide with both chromium and iron (physically mixed oxide or spinel, depending on conditions). Interestingly, on the cold rolled 316 sample we observed a “simple” chromium oxide layer on the metal substrate, similar to what is observed in the starting, uncorroded, materials (Figure 1). Our strategy is then to optimize the formation of Cr<sub>2</sub>O<sub>3</sub> in preference to spinel in LBE conditions.

Associated with the cold rolling was a decrease in the grain size in the metal in the near surface region. Grain size has been implicated in high corrosion resistance due to improved distribution of chromium in the alloy (Baer, 1980; Baer, 1981, and others).

Cold rolling also introduced linear ridges on the metal surface. Sputter depth profiling was used to determine oxide composition and when the bottoms of the etch pit were examined the cold rolled 316 was seen to have a “patchy” bottom with the patches of thicker oxide confined to the space between ridges, apparently because the failures of the oxide layer are locally confined to the region between the ridges, as compared to the smooth bottom of the etch pits on annealed 316. Mechanical stabilization of the oxide by texturing of the surface might lead to improve corrosion resistance.

Lastly, it is common to note a “smeared” region of amorphous material on the surface of samples subjected to large differential strain fields, such as are expected in cold rolling. That amorphous material should be more oxidation prone, which is consistent with our observations on the starting cold rolled material (Johnson et al., 2004, AccApp3 conference proceeding). In aluminum/steel alloys (Rawers and Mattlin 1987) this preoxidation was associated with increased corrosion resistance.

These three factors (grain size, texturing, and amorphous surface layer) have all been implicated in corrosion resistance in other environments. We propose to study well characterized samples as a function of each of these and other parameters to determine which of these factors is operative in LBE driven corrosion and so determine optimal preparation of steels for LBE service.

Further, we wish to corroborate an interesting and potentially very important result of our work: that it is possible to maintain a very stable almost pure chromium oxide protective layer in LBE under loop conditions. If we can replicate the results of the high temperature air oxidation work (Baer et al.; Davis and others) and show the applicability to LBE loops, then we might be able to raise maximum operating temperatures. Higher temperature operation will raise thermodynamic efficiencies. Our apparatus will also be able to test other alloys and ceramics for higher temperature use, up to temperatures appropriate for direct thermal hydrogen generation.

We propose a modular test facility based on stirred vessels (Figure 2) contained in a water cooled UHV chamber. Assigning the final containment and cover gas/environmental control tasks to the vacuum chamber will allow us much greater latitude in the heating, cooling, stirring, and liquid exchange tasks, and thus create an easily modified facility. The ability to change the flow, chemical, and thermal parameters will be of great utility to the process modeling community.

We envision our facility to be complementary to existing LBE test loops. Our facility is much smaller, and thus we can observe changes in the loop behavior due to perturbations (sample introduction, oxygen injection, etc.) much more easily. These changes, with the high degree of control of the loop chemistry by the use of alumina and silica in its fabrication, will allow the determination of important fundamental loop parameters (e.g. oxygen diffusivity). Further, the use of refractory oxides will allow us higher operational temperatures, limited by the operational temperature of the oxides (1400 C for alumina, 1100 C for silica). The vacuum load lock for sample introduction allows us to introduce and remove samples without stopping loop operations, allowing us to do short time exposure

experiments as well as step change experiments. Lastly, the ability to change the flow conditions independently in each region of our system allows a broad range of operational parameters to be investigated.

Los Alamos scientists have built a medium-scale LBE materials test loop (DELTA loop), and started it up in December 2001. This facility is well suited for modeling materials behavior in a fully operational loop environment. We are receiving input from the DOE scientists (in particular Ning Li) involved about the design and goals of our project.

In summary, we propose doing small scale experiments where the surface of all of the materials coming into contact with the LBE are controlled or chemically inert. Our experimental system is similar to existing reported facilities with several significant improvements which will lead to important insights into lead alloy induced corrosion in steels.

### **Goals and Objectives:**

The goals are:

- To advance the overall understanding of corrosion in lead alloy/steel systems.
- To test concepts in surface preparation and composition that have promise to greatly increase the utility of lead alloys coolants.
- To measure fundamental properties and kinetics of lead-alloy corrosion.

The objectives are

- To construct facilities to test well characterized steels in lead alloy coolant.
- To have adequate flexibility in the facility to generate useful flow, temperature, and chemistry conditions of use to the modeling community.
- To prepare well-characterized samples using insights gained from ongoing work.

### **Technical Impact:**

Although there is a vast technical literature about the conventional redox corrosion of steel (e.g., Lai, 1990; Schreier et al., 1994; Schultze, 1997; Talbot and Talbot, 1998), understanding conventional corrosion is not enough to understand the unconventional corrosion of steel by LBE. The proposed work will make a major contribution to the understanding of the mechanism of corrosion in LBE/steel systems. At the meeting of the Liquid Metal Advisory Group (August 1-2, 2002, at UNLV), representatives from LBE groups around the world (e.g., KALLA, MEGAPIE, MYRRHA) agreed on two points: (1) that basic research into corrosion in the steel/LBE system would be valuable to them, but (2) that they were not able to perform such research, because of the stringent timetable for their engineering program. Thus, the high potential yield investigation proposed here is most appropriate in the university context.

### **Facility Description:**

Our initial configuration is expected to be as follows:

#### Small Test Facility for Lead Alloy Based Coolant Technology

This facility will be a very modular and flexible tool for the investigation of lead alloy coolant materials issues and behavior.

The lead alloy coolant shall be contained in three containers (“vessels”). Each vessel will be connected to the other two (figure 2). The hot and cold section mimic the hot and cold sections of a lead alloy coolant loop. The third section will be used for composition control (e.g. oxygen control).

Each section will have an outer vessel which will be composed of alumina, a rotating displacer inside (which can be made of material under test or alumina and hold small test samples (shown)) which performs the functions of

stirring by rotating and driving transfer between the vessels by vertical translation. The heaters are located outside the vessel. The free space in the vessels (~1 cm annulus) will be filled with lead alloy coolant. Our design starts with a nominal 10cm diameter displacer with a 10 cm high and 1 cm wide annulus when the displacers are at nominal position. With these dimensions, a differential flow field of 1 m/s can be set up by rotating the displacer at 600 rpm and the lead alloy required is about 200 mL per vessel. Size of the vessels can be varied, subject to containment constraints.

The displacers can be either monolithic or composed of rings of metals under test. If rings are used, the assembly can be held in place by internal tensioning rods or welds. There will be a bottom section that can hold small samples. The vertical and rotational motion of the displacer will be controlled by a UHV compatible magnetically coupled mechanical feedthrough.

The vessels will be alumina. We will actually have two alumina crucibles, one offset inside the other. The inner crucible will be perforated to allow liquid to flow to the outer crucible. The crescent shaped annulus created will be used for instrumentation and liquid transfer functions. The inner crucible shall set the hydrodynamic environment for the test, and if required can be made of test materials if studies suggest it.

The flow in the system is controlled in an innovative way. First, the level of the LBE in each vessel is set by raising and lowering the displacers. Second, the siphons form the connecting passage between vessels: when liquid transfer is required, the siphons are connected to a lower pressure of the cover gas, and liquid metal is drawn into the siphon to the “Y” connector. At that point, the siphon activates and liquid moves from the higher level vessel to the lower level vessel. After the transfer is completed, the liquid is allowed to flow out of the siphon. Thus a controlled amount of liquid can be transferred quickly between test vessels.

The vessels will be enclosed in a stainless steel UHV ( $<10^{-9}$  torr) chamber. Holding the vessels in a vacuum chamber has several advantages. First, we can control the purity and composition of the cover gas: an important technique in oxygen control in lead alloys. Second, whatever oxygen concentration we establish in the lead alloy will also be in equilibrium with the residual cover gas; thus, we can monitor the oxidation of the *interior* of the displacers (when they are made of rings of test materials), and see effects of oxidation at the oxygen activity and temperature of the test independently of the effects of the non-isothermal lead alloy bath. Third, we will be able to exercise rigorous control over the lead alloy vapors and particulate, leading to safety advantages.

We will have a facility to extract the test samples as well as small samples of the lead alloy during operation via a vacuum load lock technique, allowing both monitoring dissolved components via standard analytical techniques and rapid sample turn-around. Windows in the vacuum chamber will allow monitoring mechanical operation and optical pyrometry. The vacuum system shall have a RGA/mass spectrometer mounted to monitor gas composition. We will have a data logging/control system that will maintain temperature, flow, composition, and safety of the test facility for unattended operation.

Oxygen control is crucial to the control of corrosion in LBE. There have been several strategies in the literature for oxygen control: gas phase loading, electrochemical cell sources, and hydrogen/water mixes. We will include the possibility of using all of these techniques, as well as using PbO or other metal oxide (perhaps at a temperature different from the main facility) as a controlled oxygen source in the third vessel. We intend to interact with the currently funded oxygen sensor project at UNLV to aid in the determination of optimal oxygen levels.

### Ion Implantation

Over the past two decades, the Farley laboratory has developed an ion beam facility capable of producing positive (or negative) ion beams, mass-selecting the ions, and studying them. Ion currents vary depending on the species, but for positive ions a typical value is a microampere, impinging on an area of a few square mm. The ion beam facility has been very productive, yielding several doctoral degrees. The facility is currently operational, and can be used by this project, which is fortunate because such facilities are either very expensive and/or time-consuming to develop. Ion beam energies are now 2 keV, but could easily be raised to larger values by biasing the sample to be implanted. Modifications of the existing apparatus are straightforward, involving the purchase of a higher-voltage

power supply and a vacuum feedthrough capable of withstanding the larger voltage. The apparatus is described in a recent publication (Mitchell, Conklin and Farley 2003, and references therein).

When ions are implanted into a solid sample, the ions have a range which varies with the energy of the ions, the mass of the ions, and the atomic mass of the target. A well-studied system is dopants into silicon, where at 50 keV, ions implant 30-170 nm into Si. For our research program, measurement of the range of implanted ions in steel will be our first experiment. Back-of-the-envelope calculations indicate that to implant enough ions to label several mm<sup>2</sup> of sample requires only one minute at an ion current of one microamp.

We plan experiments in which we implant ions into the steel sample, and then we measure the position of the material in the sample by using the SIMS-TOF experimental apparatus at the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory. In the TOF-SIMS (time of flight-secondary ion mass spectrometer), the surface is stripped off using ion etching, and the resulting ions are mass-analyzed using a time of flight (TOF) spectrometer. The result is very sensitive measurement of the depth of ion implantation. Subsequent experiments shall measure the movement of the implanted material due to test conditions.

### **Measurements Planned and Possible:**

- We will expose well-characterized metal samples to LBE and other lead alloys under non-isothermal and oxygen control conditions. We do this by having three independently heated vessels connected by siphons, so that lead alloy from the hot region can be displaced into the cold region, and vice versa. The samples will be investigated as we have done previously.
- We will investigate the response of the system to step changes in composition (i.e., oxygen concentration) to get diffusion and dynamic measurements.
- We will investigate the movement of stable isotope labels ion-implanted in the steels, and determine diffusion rates of these components of the steels.
- We will extract lead alloy samples and measure dissolved and particulate concentration as a function of operation parameters.
- We will examine the effect of our mixing geometry. We might see greater corrosion due to flow impacting the samples mounted on the vessel as versus the displacer walls. Additionally, samples may be influenced by any particle production due to metal oxide formation. If these particles do not dissolve in the hot region, they may build up and affect oxide stability.
- We will try oxygen sensors and oxygen control technology as they become available.
- Other process parameters can be modeled using changes in facility geometry.

### **Human Resources:**

We have the collaboration of all of the participants of the analysis proposal (which see). In particular:

- Dale Perry is an expert in lead, and will be very helpful in the planning of the facility and analysis of our results.
- Ning Li and UNLV workers (e.g., Samir Moujaes) will be useful in modeling the flow and dynamics of our facility as well as helping guide the research into useful directions.
- We have an ongoing collaboration with Eric Loewen of INEEL, who has done LBE corrosion work with a small facility at INEEL.

**Institutional Resources:**

We have at UNLV an active program in LBE research, and a growing program in materials science. As such, we have access to XPS, SEM, atom probes, TEM (planned), ICP analysis, Raman, IR microscopy, X-ray powder diffraction, and other analytical techniques.

We have a space in the Chemistry building, UNLV, which will be dedicated to lead activities. It has an independent fume hood system, is located at ground level, and is controlled by three sequential independent locking systems to the outside. Thus, it is very well suited for the intended task.

We also have at UNLV a water cooled UHV system currently not being utilized. This is an ion/turbo pumped system, and will be used to fabricate the STFLACT. The replacement cost of such a system would be on the order of \$30K-40K.

We have the mass selected ion system in the Physics department, UNLV. This will be upgraded (sample holding stage fabricated, bias voltage supply purchased) to do sample modification using ion beams work.

We have existing vacuum equipment and infrastructure (pumps, mass spectrometers) which shall be used to set up the controlled atmosphere tube furnace facility for sample preparation.

We have an active experimental proposal at the Environmental and Molecular Sciences Laboratory (EMSL) operated by Battelle which will be used to do further analyses of our samples and in particular where SIMS investigations of the ion modified surfaces (e.g. the stable isotope labels) will be conducted.

**Statement of Work/Time Line for Year 1 and Later:**

We will start this project Spring 2004. We will have the full time efforts of Umar Younas, and Ho Trung Thao in building the Small Test Facility for Lead Alloy Coolant Technology (STFLACT). Dan Koury and Brian Hosterman will continue their work on the characterization of exposed samples.

Initial efforts will be to adapt the UHV system to the planned work (install new ports, fabricate experimental stand, etc.). Installation will be in the Chemistry Building, UNLV.

Early work with LBE will include test of thermal and chemical instrumentation and control and measurement of fundamental parameters, such as viscosity and stability of the thermal and chemical controls.

We will look at short-term experiments (impulse response of the system, short exposure materials samples) after the establishment of a controllable thermal and chemical environment. It is very important to note that we will be able to do quick turn-around experiments. Locating the sample exposure facility near the people doing analysis allows rapid feedback between the preparation and analysis of samples.

Once operation is routine (expected 9-12 months into the project), we will start extended duration materials tests.

We will start the fabrication of a second system dedicated to long term studies; effort to run into year 2.

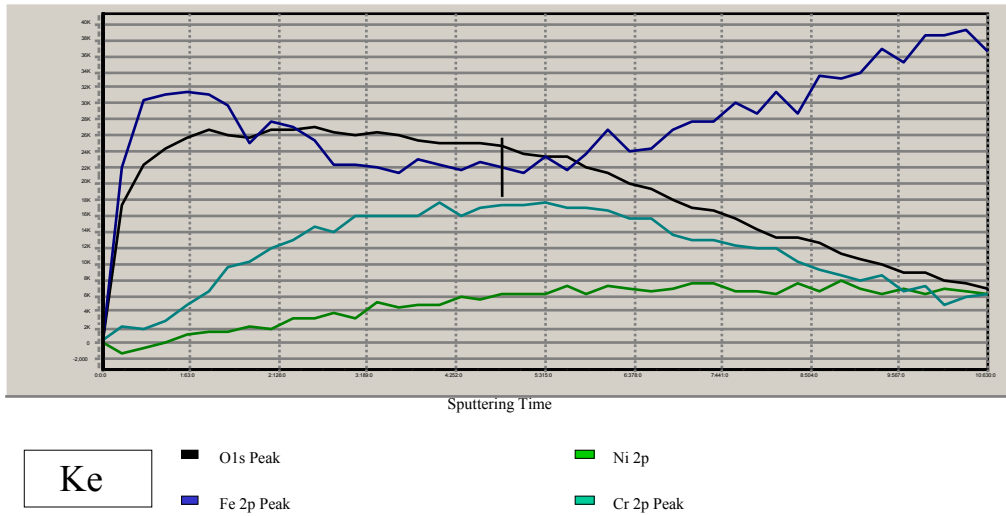
Studies driven by our results in years 1 and 2 as well as long term studies will continue into year 3.

**Deliverables:**

- Small Test Facility for Lead Alloy Coolant Technology (STFLACT).
- Test samples characterized before and after both long term and short term exposure to lead alloy loop environment for analytical studies (months 9 forward).

- Test systems for hydrodynamic/thermal/chemical modeling studies (months 6 forward).
- Journal article on the STFLACT facility (end of year 1).
- Papers on the analytical and modeling studies to be presented at conferences, reviews, and in the literature (years 1 and later).
- A second test facility for long term studies (year 2). A Master thesis based on the facility development (2004-5), and continued graduate student involvement.
- Continued collaboration with LBE research efforts. These include: (a) other LBE efforts at UNLV (e.g., the effort in hydrodynamic flow simulations by Samir Moujaes), (b) DOE scientists at Los Alamos (especially Ning Li of Los Alamos and his postdoc, Jinsuo Zhang) and elsewhere, (c) Eric Loewen at INEEL, and (d) international LBE partners working on projects such as KALLA, MEGAPIE, MYRRHA, IPPE.
- Progress reports at regular intervals (monthly, quarterly, semi-annual, and annually) to support UNLV reporting to the DOE AFCI program.
- Final report.

XPS Depth Profile of annealed 316 Stainless Steel  
Exposed to LBE for 1000 hrs and 550 C



Note enhancement of Fe and O at surface ( $\text{Fe}_2\text{O}_3$ ) over a layer of Fe and Cr oxides (spinel) indicating a “complex” oxide.

Figure 1 Depth profiles of annealed and cold rolled 316, showing different oxide structures.

## Small Test Facility for Lead Alloy Coolant Technology (block diagram)

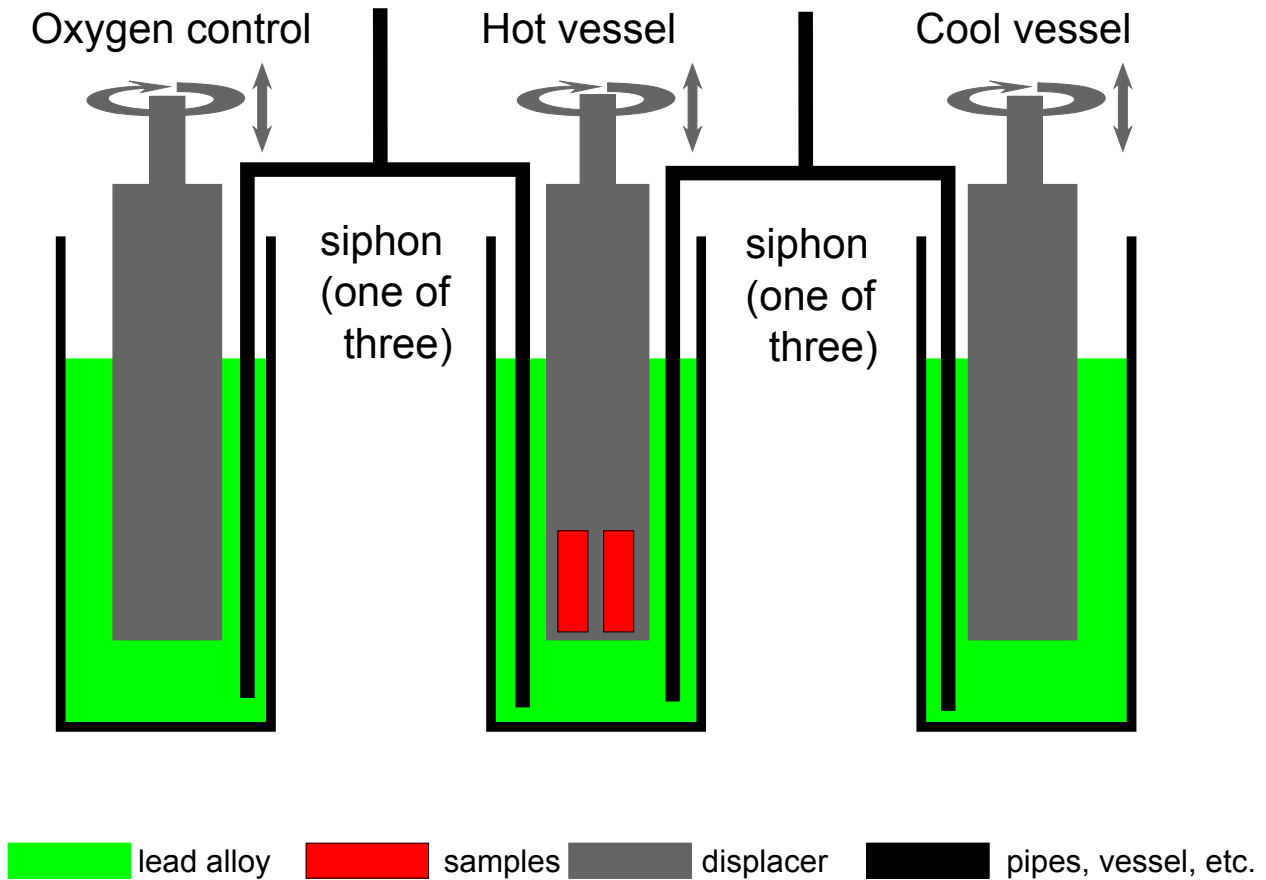


Figure 2 Block diagram of Test Facility. Siphons are used to transfer liquid from one vessel to another, controlled by the level set by the vertical movement of the displacers. Liquid velocities inside each vessel are set by the rotational motion of the displacer.

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