Lawrence Livermore Laboratory

Materials Development for Thermochemical
Cycles: Sulfuric Acid Vaporizer. Semi-
Annual Technical Report for 1 October 1977
through 31 March 1978.

Oscar H. Krikorian

June 22, 1978

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Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

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ABSTRACT

Installation of a sulfuric acid corrosion test facility has been completed and is herein described. It is awaiting final checkout and approval by Mechanical Engineering and Hazards Control. The facility is to be used for testing of potential materials for containment and heat exchange of a sulfuric acid vaporizer at temperatures up to 725K and boiling pressures of 20 atm (2 MPa). Materials that are ready for test are Duriron, Durichlor 51, single crystal Si, hot-pressed Si_3N_4 (Noralide NC-132), and hot-pressed SiC (Crystar HD-435), and tests are expected to get underway in April pending Hazards Control approval.

INTRODUCTION

A study is underway at the Lawrence Livermore Laboratory to test and evaluate materials for a sulfuric acid vaporizer under conditions that simulate actual operating conditions for the thermochemical hydrogen cycles under study at the General Atomics and Westinghouse laboratories. It is expected that an azeotropic composition of ~97-98 weight % H_2SO_4 will be vaporized in these cycles at pressures of ~4-20 atm (0.4-2.0 MPa) and boiling points of about 634-725K. We expect to study both the amount of corrosion and the nature of attack of available and potential containment materials for boiling sulfuric acid to gain an understanding of corrosion mechanisms and materials limitations.

The known technology on sulfuric acid^(1,2,3) indicates that only three materials - gold, platinum, and glass - are resistant to corrosion under

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the operating conditions. Gold and platinum are too expensive for use in quantity in this application, and glass is both fragile and restricts heat transfer. Another class of materials - the high silicon cast irons - is known to have low corrosion rates in boiling 98% sulfuric acid up to 611K, and has been used at temperatures as high as 811K, although the corrosion rate is not reported for these higher temperatures.⁽¹⁻⁴⁾ Three commercial high silicon cast iron alloys are produced in this country: Duriron, Durichlor 51, and Superchlor. These alloys all contain 14.5% Si, 0.85% C, and 0.65% Mn. In addition Durichlor 51 and Superchlor also contain 4.5% Cr. The main difference between Durichlor 51 and Superchlor is that Superchlor has undergone vacuum treatment and possesses a higher strength than Durichlor 51. The high silicon cast irons have serious limitations as engineering materials because of low tensile strength, poor ductility, poor impact resistance, and poor fabrication characteristics. If, however, their corrosion resistance proves out, they would serve as suitable materials for the initial laboratory phase of cycle development. We therefore plan to test the corrosion resistance of Duriron and Durichlor 51 (Superchlor is presently not available) as an initial aspect of our study.

For commercial applications, two types of materials need to be considered: (1) conventional alloys coated or clad with corrosion resistant materials, and (2) ceramic materials. From the standpoint of a shorter term development, the coated alloys present the greater promise; whereas from the standpoint of a more durable material, but with longer term development and fabrication problems, the ceramics are more promising. Metal alloys that can be considered as suitable base materials for coatings are those that already have some corrosion resistance to sulfuric acid and otherwise have good engineering properties for fabrication as heat exchanger and container materials. These include the Fe-Cr, Fe-Cr-Ni, Ni-Cr, Ni-Cr-Mo base alloys, and the refractory metals Mo, Nb and Ta. We believe that high silicon content coatings^(5,6) would provide the optimum protection for these alloys, since a protective SiO_2 layer is expected to form in these coatings, and SiO_2 glass is known to be resistant to attack by H_2SO_4 . We believe that CrSi_2 is a good candidate

as a coating material for the iron and nickel base alloys because its thermal expansion coefficient is very close to that of the alloys. For the refractory metals, NbSi₂ or TaSi₂ coatings should be considered since such coatings have been reported to exhibit ductility in thicknesses of ~100μm.⁽⁶⁾ We plan to test the corrosion resistance of CrSi₂ to H₂SO₄, and if time is available, to coat some alloy coupons with CrSi₂ and test them as well. We also plan to conduct H₂SO₄ corrosion tests on single crystal Si, and on high density hot-pressed Si₃N₄ and SiC to determine the inherent corrosion behavior of these ceramic materials.

In addition to materials characteristics, we need to consider chemical approaches that can be used to limit corrosion, that is, the use of inhibitors. Inhibitors may consist of salts dissolved in the H₂SO₄, saturated solid additives such as sulfates, and gaseous additives. Inhibitors may have effects such as improving the characteristics of protective surface coatings, reducing material dissolution rates, or reducing the oxidizing characteristics of the H₂SO₄. A promising approach here is to use gaseous SO₂ as an additive to reduce the amount of O₂ produced by decomposition in the boiling H₂SO₄, i.e., the equilibrium, $\text{H}_2\text{SO}_4 = \text{H}_2\text{O} + \text{SO}_2 + 1/2 \text{O}_2$, would be shifted to the left by the law of mass action. We expect to conduct tests using SO₂ as an additive inhibitor if, as the testing program develops, it appears that materials show sufficient promise to warrant them.

The main effort during the first 6 months of this project has been on the design, fabrication, and check-out of an H₂SO₄ test facility for the static testing of specimens for corrosion in liquid H₂SO₄ at temperatures of 634-725K and pressures of ~4-20 atm (0.4-2.0 MPa). We have also acquired and prepared specimens of Duriron, Durichlor 51, single crystal Si, hot-pressed Si₃N₄ (Noralide NC-132) and hot-pressed SiC (crystar HD-435) for testing.

H₂SO₄ CORROSION TEST FACILITY

The facility for conducting static tests in liquid H₂SO₄ was completed in February. Operation of the unit has been delayed however until final pressure inspections, engineering safety calculations, and operating procedures

have been completed and checked by Hazards Control. It is now anticipated that testing of specimens should be underway in April.

A schematic illustration of the test facility and of the autoclave chamber is shown in Figures 1a and 1b. The entire facility has been installed in a hood for safety reasons, and has been engineered with a minimum safety factor of 4 for pressure containment using up to 50 atm (5 MPa) Ar overpressure in the system at a temperature of 725K. A double-walled blast shield filled with sand between the walls is used for additional safety.

Pure fused silica vials will be used for primary containment of the sulfuric acid and test specimens. For the initial corrosion tests H_2SO_4 will be taken directly from a bottle of concentrated reagent grade 95-98 wt% H_2SO_4 . A weighed 10g quantity of the H_2SO_4 will be placed in a silica vial along with a rod-shaped test specimen of sufficient length (60-70 mm) to protrude above the liquid surface. The bottom of the vial will then be chilled with liquid nitrogen, and the vial evacuated and sealed off with a torch. The vial will then be placed inside of a stainless steel test tube, and six such sample tubes placed in the autoclave (see figure 1b). A silica liner inside the autoclave and a stainless steel shield placed above the test tubes, will function (along with the stainless steel test tubes) as secondary containment for the H_2SO_4 in case of breakage of any of the sample vials.

The autoclave (Autoclave Engineering, Inc. Model No. BC-1005A) is made of SA-182-F316 steel and has a chamber cavity 76 mm i.d. x 230 mm high. Temperatures are measured with a sheathed chromel-alumel thermocouple and argon gas is introduced into the autoclave chamber through an annular tube surrounding the thermocouple. During a run, a static argon overpressure of about 4-5 atm (0.4-0.5 MPa) in excess of the vapor pressure of the H_2SO_4 within the vials will be maintained in order to keep the silica under compression and minimize the likelihood of breakage. A cylindrical heater is provided for the sides of the autoclave and flat heaters for the top and bottom to permit careful control of the temperature profile. It is

actually desirable for the static tests to have a slightly higher temperature at the top to prevent refluxing. Typically, we expect to keep the top of the autoclave about 7K hotter than the bottom, and temperature profile scans have shown that this can be achieved.

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Figure 1a. A schematic view of the H_2SO_4 Corrosion Test Facility.

Figure 1b. A schematic view of the autoclave showing location of a typical sample vial. A total of 6 vials are contained in the autoclave grouped in a circle surrounding the thermocouple.