Commercial Alloys for Sulfuric Acid Vaporization in Thermochemical Hydrogen Cycles

Thomas M. Lillo, *Karen M. Delezene-Briggs, Material Sciences, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2218*

Abstract

Most thermochemical cycles being considered for producing hydrogen include a processing stream in which dilute sulfuric acid is concentrated, vaporized and then decomposed over a catalyst. The sulfuric acid vaporizer is exposed to highly aggressive conditions. Liquid sulfuric acid will be present at a concentration of >96 wt% (>90 mol %) H_2SO_4 and temperatures exceeding 400°C [Brown, et. al, 2003]. The system will also be pressurized, 0.7-3.5 MPa, to keep the sulfuric acid in the liquid state at this temperature and acid concentration.

These conditions far exceed those found in the commercial sulfuric acid generation, regeneration and handling industries. Exotic materials, e.g. ceramics, precious metals, clad materials, etc., have been proposed for this application [Wong, et. al., 2005]. However, development time, costs, reliability, safety concerns and/or certification issues plague such solutions and should be considered as relatively long-term, optimum solutions. A more cost-effective (and relatively near-term) solution would be to use commercially-available metallic alloys to demonstrate the cycle and study process variables. However, the corrosion behavior of commercial alloys in sulfuric acid is rarely characterized above the natural boiling point of concentrated sulfuric acid (~250°C at 1 atm). Therefore a screening study was undertaken to evaluate the suitability of various commercial alloys for concentration and vaporization of high-temperature sulfuric acid. Initially alloys were subjected to static corrosion tests in concentrated sulfuric acid (~95-97% H_2SO_4) at temperatures and exposure times up to 200°C and 480 hours, respectively. Alloys with a corrosion rate of less than 5 mm/year were then subjected to static corrosion tests at a pressure of 1.4 MPa and temperatures up to 375°C. Exposure times were shorter due to safety concerns and ranged from as short as 5 hours up to 144 hours. The materials evaluated included nickel-, iron- and cobalt-based commercial alloys.

The corrosion rates in these tests are reported and how they may or may not relate to the corrosion behavior in an operating thermochemical cycle is discussed.

Introduction

The economical generation of large quantities of hydrogen is the first challenge for a hydrogen economy. One promising method being explored is through thermochemical hydrogen cycles, i.e. splitting water molecules through a series of chemical reactions to produce hydrogen and oxygen. Only water is input into these cycles - the other chemical species that participate in various chemical reactions are simply recycled. The advantage is that the temperatures required are much lower than those in thermolysis of pure water (700-900°C for thermochemical cycles versus >2500°C for thermolysis [Brown, et. al., 2000]). However, many of these thermochemical cycles are based on the generation and subsequent decomposition of sulfuric acid. In the Sulfur-Iodine (S-I) cycle, pioneered by General Atomics in the 1980's, sulfuric acid exists over a range of concentrations, temperatures and pressures in various steps of the S-I cycle. Dilute sulfuric acid is generated initially in the Bunsen reaction where water is reacted with SO_2 and I_2 gases to produce sulfuric and HI_x acids. The acids are separated and processed separately from this point forward. Sulfuric acid at a concentration of ~57 wt% H_2SO_4 is passed to a concentration phase where it exits at ~98 wt% H_2SO_4 [Brown, et. al, 2003]. In the process the temperature is also increased from ~120°C to ~411°C at pressures up to ~3.5 MPa. The acid is then vaporized and heated to 800-900°C and passed over a catalyst to produce SO_2, H_2O and O_2. The oxygen is removed and the SO_2 along with residual water is recycled to start the process over again.

Liquid sulfuric acid (~57-98 wt% H_2SO_4) at temperatures up to 400°C presents a serious corrosion issue. In the S-I cycle, liquid sulfuric acid exists at temperatures and pressures not normally encountered in industrial practice. Generally, corrosion data for materials are only given at temperatures up to the boiling point at atmospheric pressure (~250°C). The present application requires pressures above atmospheric to achieve high cycle efficiencies (~40-50%). General Atomics surveyed a host of materials some 20+ years ago [Trester, et. al., 1981]. Their conclusion was that a combination of glass lined steel, plastics, precious metal coatings/claddings, high silicon alloys and ceramics, especially silicon-based materials such as silicon carbide, could be used at various points in the concentration and vaporization section to reduce corrosion rates to an acceptable level. Coatings and brittle materials (ceramics and high silicon alloys) are particularly troublesome from a safety standpoint. New alloys have been developed during the intervening years for other applications that may hold promise of low corrosion rates in sulfuric acid with reasonable ductility. This work reports the results of initial screening corrosion studies to identify materials that might be used in construction of the sulfuric acid vaporization section of the S-I cycle. The relevant conditions are ~411°C, 1.4 MPa at a sulfuric acid concentration of 96-98 wt% H_2SO_4.

Experimental Procedures

Various commercially-available alloys were acquired and subjected to static corrosion tests. Samples were categorized into various classes based on their composition and are shown in Table 1. Small samples were cut from the parent material using an abrasive cutoff wheel. The samples were further ground to obtain parallel sides. All surfaces were ground to remove surface layers, impurities and/or contamination from commercial alloy fabrication processes. The sample size ranged from 0.05 – 3.0 grams and had a total surface area of approximately, 0.3-5 cm^2. Initial sample weights were recorded to $\underline{+}0.0001$ grams.

Corrosion testing was carried out in two phases. The first phase was performed to screen out materials that were unsuitable for use with sulfuric acid. These tests were conducted in static sulfuric acid (96-97 wt% H_2SO_4) at 200°C under atmospheric pressure. Mantle heaters were used to heat flasks containing up to 100 ml of acid (ratio of acid volume to surface area ~1 mL/mm^2). The temperature was measured with a thermometer and held within ±5°C. The flasks were equipped with a reflux condenser to prevent loss of water vapor and changes to the sulfuric acid concentration. Tests were run for 24 to 480 hours after which the apparatus was cooled and the samples rinsed, cleaned and reweighed. The samples were cleaned with Ox-Out 536, Scale & Oxide Remover for Stainless Steel and Aluminum, (ChemClean Corporation). Cleaning was carried out according to ASTM Standard G-1. The corrosion rate was calculated and plotted as a function of exposure time.

Materials that exhibited corrosion rates of less than 5.1 mm/yr during the first phase of corrosion testing were included in the second phase of testing which entailed testing at high pressure (~1.4 MPa) and temperatures up to ~375°C. The increased pressure kept the sulfuric acid in the liquid phase even at the high test temperatures. Corrosion testing these conditions required the use of specialized testing equipment. The equipment used in this study consisted of a standard pressure vessel capable of 600°C and 41 MPa with a 500 ml internal cavity. The equipment was purchased from Parr Instruments and was fabricated from alloy C-276. This alloy is not sufficiently corrosion resistant to withstand direct contact with liquid sulfuric acid at high temperature so an inner, covered vial of quartz was made to isolate the acid from the container wall. A schematic of the experimental set up is shown in Figure 1. Some vapors still escaped the quartz vial so the pressure vessel was also coated with silicon in an effort to generate a SiO_2 coating that would protect the vessel walls. The silicon coating was applied by Restek Corporation. using a CVD process. The coating increased the corrosion resistance to an acceptable level. However, a defect or scratch in the coating due to repeated sample loading and unloading of the vessel resulted in the need to occasionally recoat the vessel, illustrating the main draw back with the use of coatings to obtain corrosion resistance. Additionally, corrosion was also minimized by placing activated carbon around the quartz tube which acted to neutralize sulfuric acid vapors that escaped from the covered quartz tube.

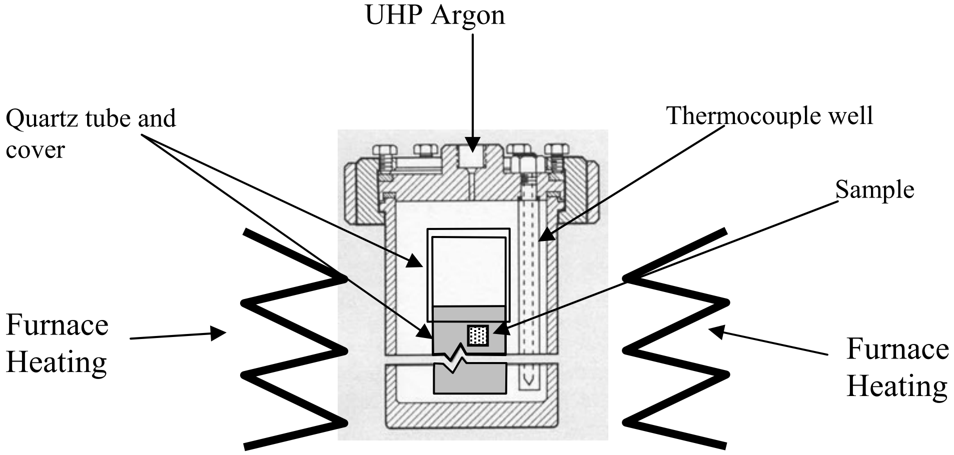


Figure 1. High temperature and pressure experimental set up. The sample resides in an inner quartz container that prevents the acid from contacting the pressure vessel walls.

The inner quartz vial was filled with up to 40 ml of sulfuric acid. In the case of small samples, the sample was placed on a bed of small beads to allow circulation of the acid around the sample during the experiment. Larger samples were leaned against the inner wall of the quartz vial to allow circulation of the acid around the entire sample. The ratio of acid volume to surface area was on the order of ~0.2 mL/mm^2. The sample was completely immersed in acid during the entire experiment. The vessel was purged with ultrahigh purity argon and maintained between 1.4-2.1 MPa. The temperature was maintained within $\pm 5^oC$ by a single setpoint controller. Test duration was approximately 5 hours initially with longer duration tests ($\geq$140 hours) performed once a material demonstrated reasonable corrosion resistant in the short duration tests.

After testing, samples were weighed, photographed and prepared for metallographic examination. In some cases the samples required cleaning to remove corrosion layers in order to determine the weight change and calculate an accurate corrosion rate. Corrosion tests were repeated for materials exhibiting corrosion layer formation. These duplicate samples were not cleaned but were prepared for SEM analysis of the corrosion products.

Results

Corrosion tests at atmospheric pressure - Numerous commercial alloys were screened in the atmospheric corrosion tests at 200^oC for exposure times up to 480 hours. A partial list is shown in Table 1 along with the apparent corrosion rate for atmospheric corrosion tests performed at 200^oC.

Table 1. Alloy Screening List

Alloy	Exposure time, hours	Corrosion Rate, mm/yr (mils/yr)
C-22, nickel-based alloy	96	10.0 (392)
I-800 nickel-based alloy	96	3.1 (122)
I-617 nickel-based alloy	72	8.0 (315)
Hastelloy D-205 nickel-based alloy	120	2.1 (83)
Hastelloy B3 nickel-based alloy	72	4.4 (172)
MP35N, cobalt-based alloy	72	8.9 (351)
Ti-6Al-4V, titanium-based alloy	96	3.0 (117)
AL610, iron-based alloy	120	2.5 (99)
418, Stainless steel	96	5.8 (228)
430, Stainless Steel	96	1.8 (71)
440C, Stainless Steel	96	3.3 (129)
446, Stainless Steel	96	2.0 (78)
Zecor, iron-based	96	2.0 (80)
Saramet #23, iron-based	384	0.9 (34)
Saramet #35, iron-based	480	0.8 (30)

Generally, all alloys exhibited very high corrosion rates initially and then decreased toward a steady-state corrosion rate, Figure 1. The corrosion rate steadily decreases as a protective film is formed. In general, the iron-based alloys performed better nickel-based alloys, although Hastelloy D-205 exhibits a corrosion rate comparable to the iron-based alloys. Alloy D-205 has a relatively high (~5 wt%) silicon content compared to the other nickel-based alloys and is on the order of the more corrosion resistant iron-based alloys, e.g. Saramet #23, #35 and Zecor. Table 1 seems to indicate that titanium alloys may also offer the reasonable corrosion resistance. The last three alloys in Table 1 were specifically developed for use in

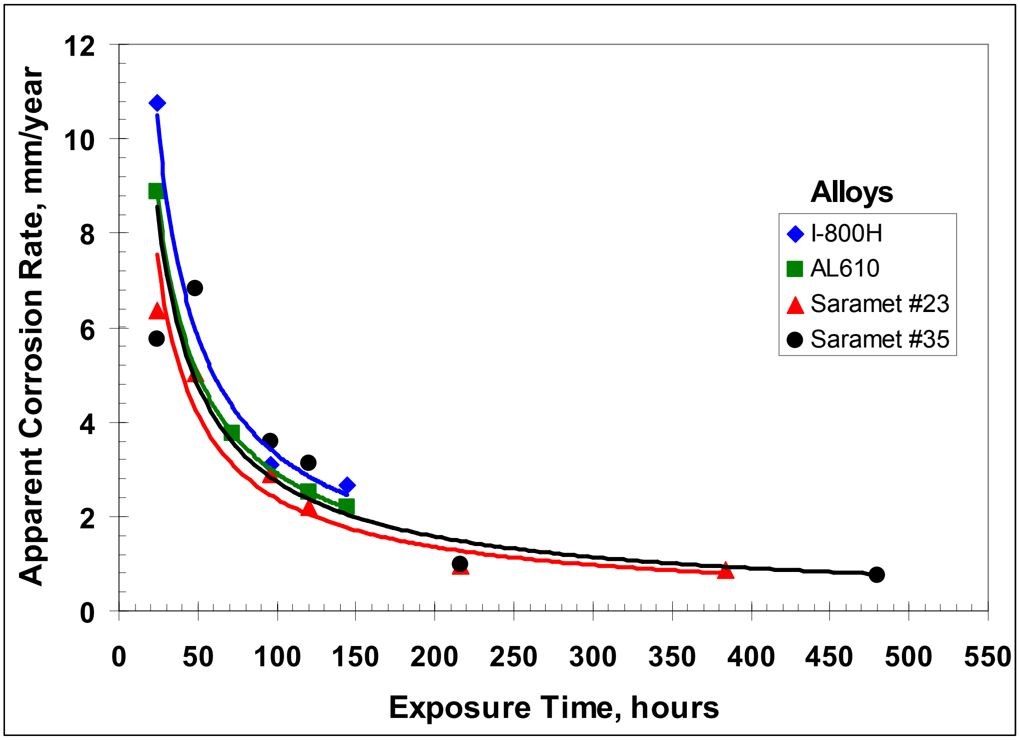


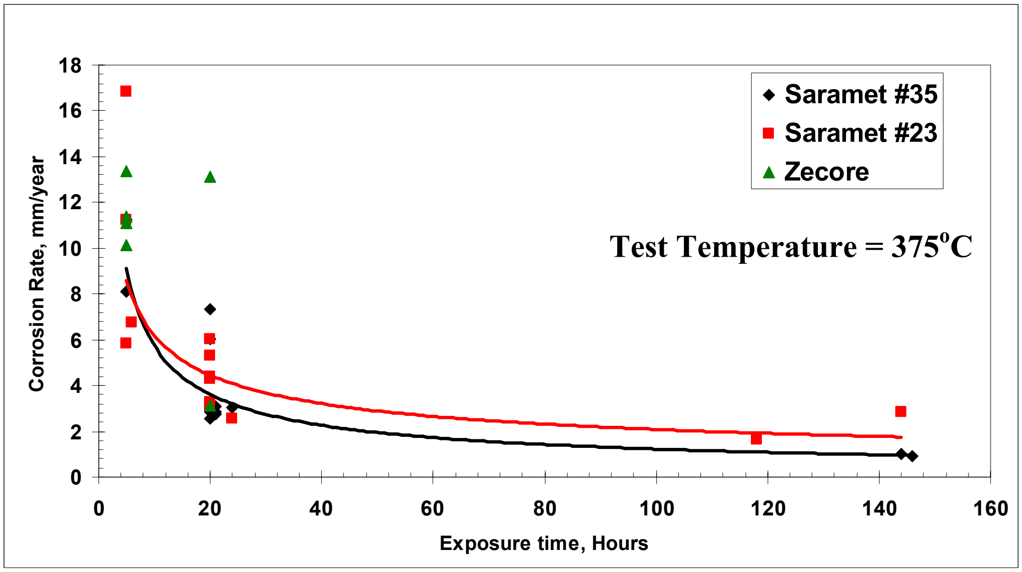
Figure 1. Corrosion rate of selected alloys as a function of exposure time, Conditions: 96 wt% H_2SO_4 at 200°C and atmospheric pressure.

commercial applications where liquid sulfuric acid is present at elevated temperatures. However, the temperature our intended application far exceeds their intended use. These alloys also exhibit good formability in addition to corrosion resistance in concentrated sulfuric acid. Since there is commercial experience with these alloys they were passed to the pressurized sulfuric acid corrosion tests. Other alloys in Table 1, e.g. D-205, AL610, Ti-6Al-4V, 430 stainless steel and 446 stainless steel, show promise but have not yet been fully characterized in the pressurized corrosion tests.

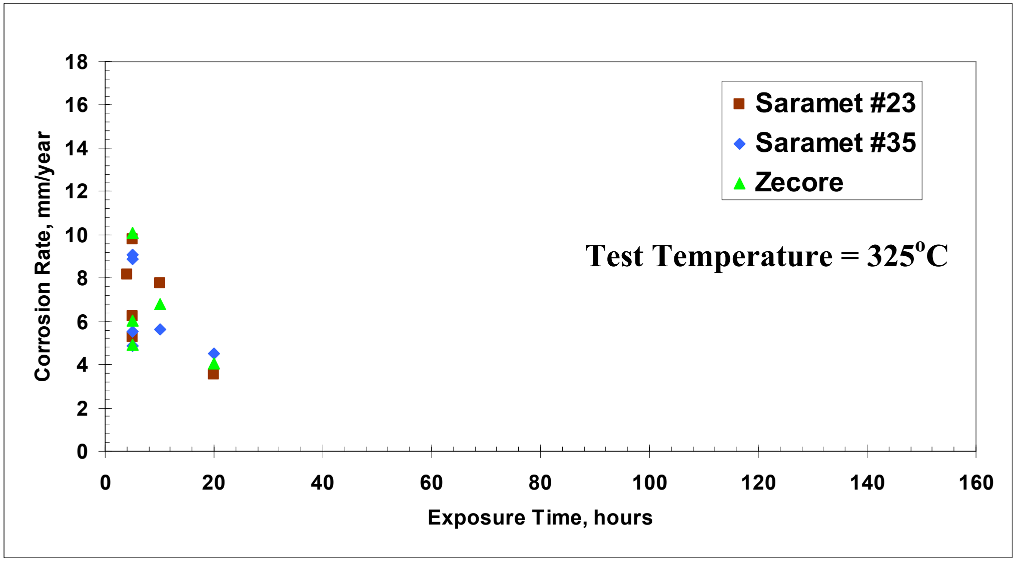
Pressurized corrosion tests - Temperatures in the pressurized corrosion tests were significantly higher (up to 375^{o}C) than in the atmospheric corrosion screening tests. Space in the pressure vessel was limited, requiring the samples to be quite small. However, efforts were made to ensure that the liquid volume to surface area exceeded 0.2 ml/mm^2 as specified by ASTM Standard G 31, Standard Practice for Laboratory Immersion Corrosion Testing of Metals.

Testing is ongoing and only two temperatures have been explored to some extent, so far. The initial results for Zecor, Saramet #23 and Saramet #35 are shown in Figure 2. At 375^{o}C and 1.4 MPa, Figure 2a, corrosion rates in 96 wt% H_2SO_4 are initially high and, as with testing at 200^{o}C, decrease toward steady state values at longer exposure times. Short exposure times resulted in considerable scatter in the calculated corrosion rate and is due to difficulties in determining when the sample was actually at the test temperature (a thermocouple well in the pressure vessel was located near the sample but not in direct contact with either the sample or the quartz container holding the sulfuric acid). Also transient corrosion behavior represented a major portion (if not all) of the calculated corrosion rate and is sensitive to temperature and sample preparation. Of the alloys tested so far, Saramet #35 exhibits the lowest steady state corrosion rate at ~ 0.9 mm/yr (36 mils/yr) (although the corrosion rate appears to be still decreasing even after 144 hours of exposure). The corrosion behavior of alloy, Zecor, seems to resemble that of Saramet #35 but this alloy has not yet been subject to long term exposures. (The corrosion behaviors of these alloys are expected to be similar since they have similar compositions.) The corrosion resistance of these three alloys is thought to arise from the relatively high silicon content, 4-6 wt% Si, which results in the development of a protective SiO_2 film on the sample surface. Figure 3 shows a cross section through a Saramet #23 corrosion sample and the surface film that developed. The top layer was found to contain a high amount of sulfur while the layer next to the base metal was found to be enriched in silicon, presumably in the form of SiO_2. Quartz is known to be highly corrosion resistant to sulfuric acid at high temperatures [Kubo, et. al., 2004] and, therefore, materials that form a SiO_2 layer are expected to possess significant corrosion resistance. For instance, silicon carbide is has also been found to be highly corrosion resistant to high temperature sulfuric acid [Wong, et. al., 2005]. However, the Si-rich layer next to the base metal in this study is seen to contain cracks and there is evidence of a gap at the interface. Although these may have arisen from sample preparation, further efforts will be necessary to evaluate the integrity and very long-term (>1,000 hours) stability of this surface film.

Less scatter is observed in the corrosion data of Figure 2b for the 325^{o}C corrosion tests and is a result of improved experimental design and control. The trend with increasing time appears to be similar, i.e. decreasing corrosion rate, to that observed at 375^{o}C, although long term exposures have not been performed. The behavior of all three alloys is very similar at this lower temperature and no alloy exhibits a clear benefit from a corrosion standpoint. Again, extended exposure times may reveal differences between these alloys.



a)



b)

Figure 2. Corrosion behavior of selected alloys at a) 375°C and b) 325°C in 96 wt% H_2SO_4 at 1.4 MPa.

Discussion

As mentioned the main goal of this work is to determine whether commercial metallic alloys can be used in a sulfuric acid decomposition demonstration loop. Metallic alloys tend to exhibit substantial ductility and, *generally,* do not to fail in a catastrophic manner. Metallic alloys also are more readily formed into useful shapes than brittle materials such as ceramics. The obvious tradeoff is in the corrosion resistance of the components. Use of metallic materials will require tolerance of some corrosion products in the sulfuric acid processing stream. The level of corrosion products that can be tolerated cannot be answered at this time. Therefore, materials with the lowest apparent corrosion rate have the greatest potential for use as structural components. However, a system will need to be constructed and operated to determine whether the corrosion resistance attained is within acceptable limits.

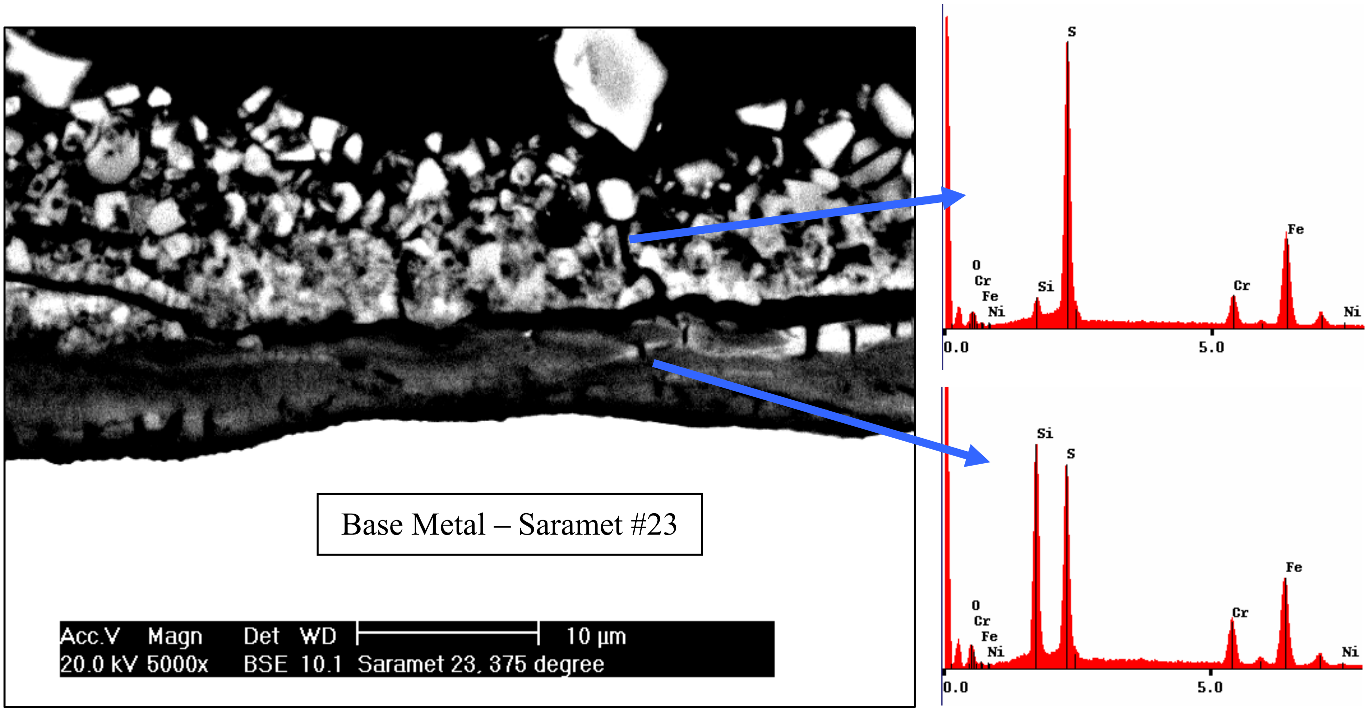


Figure 3. Cross section through the surface film that formed on a Saramet #23 sample exposed to sulfuric acid at 375°C.

The materials of this study would seem to indicate that corrosion rates on the order of 0.5-0.8 mm/yr can be expected at long exposure times (>150 hours). Generally the chemical industry specifies a corrosion rate of less than 0.1 mm/yr as acceptable for most applications. It is possible that one or more of the alloys in this study may attain this corrosion rate at very long exposure times, especially if the corrosion rate continues to decrease with increasing exposure time. However, as pointed out in the results, the *initial corrosion rate* is *very* high. Initial operation of a metallic system will result in high levels of corrosion products in the processing stream. *Therefore, a system constructed from metallic materials would have to be "seasoned" for periods up to 100 hours or longer to form protective films and obtain reasonably low possible corrosion rates.*

It also must be pointed that the corrosion behavior of materials in a flowing system may be very different than shown in these static corrosion tests. Component materials would experience a continuous flow of "fresh" sulfuric acid in the target application - a continuously operating sulfuric acid decomposition loop. Hopefully the ratio of the volume of sulfuric acid to the surface area of the sample in this study (0.2 ml/mm^2) is large enough to approximately simulate continuous exposure to fresh sulfuric acid. (However, recent literature suggests much higher values, ~1 ml/mm^2 [Rodda, et. al., 2003], are needed.) However, the sulfuric acid is flowing in the target application and this has not been simulated in the experiments of this study. Loose corrosion products may build up on the sample surface and interfere with further corrosion, e.g. the outer corrosion product layer seen in Figure 3, under the static conditions of this study. In a flowing environment, loose corrosion products may be swept away and promote higher corrosion rates. Furthermore, static conditions allow the build up of soluble corrosion products that may interfere with further corrosion. Since the initial corrosion rates observed in this study are very high, all the experiments in this study probably concluded with metallic ions concentrations that greatly exceeded 10 mg/L.

Although the corrosion rates in an operating sulfuric acid decomposition loop may be different than those found in the experiments reported here, screening corrosion tests such as these are still the best method of identifying promising materials of construction. Once promising materials of construction are identified a flowing corrosion loop can be constructed to assess corrosion behavior under dynamic conditions. If it is found that the corrosion rate is still too high, these materials still may be used as base materials on which corrosion resistant coatings may be applied. In case the coating is breached the base material would still have a reasonable amount of corrosion resistance, allowing time to discover and safely repaired a breach in the coating. In fact this has been the strategy used for the pressure vessel in these experiments. As mentioned, the internal surfaces of the vessel have been coated with a silicon coating (Restek) to generate a protective barrier between any spurious sulfuric acid vapors and the vessel walls to minimize corrosion of the vessel. However, the vessel occasionally needs to be re-coated since some damage to the coating occurs during loading and unloading of the samples in the vessel. The underlying base metal (alloy C-276) affords some corrosion resistance. Corrosion damage is minimal and does not affect the mechanical integrity of the vessel significantly.

Summary and Conclusions

Preliminary static corrosion, screening tests have identified potential metallic alloys for use in the construction of a sulfuric acid decomposition loop. The corrosion rates of three commercially-available alloys, Saramet #23, Saramet #35 and Zecor, are found to approach those accepted by the chemical industry, ~0.1 mm/year. These iron-based alloys have relatively high silicon contents and the protective surface film that develops is rich in silicon, probably SiO_2. However, much longer exposure tests are needed to verify that the protective surface films that initially form are stable and not prone to spalling. Regardless of the long term corrosion rate, the *initial* corrosion rate is quite high. Therefore, any components made from these alloys will have to be "seasoned" in sulfuric acid at elevated temperatures prior to use to prevent unacceptable levels of corrosion products in the process stream. Finally, other nickel-based and titanium-based alloys need further characterization to assess their potential for use as structural materials.

Also, it is noted that the static corrosion rates determined in this study may be much lower than in flowing systems. Loose corrosion products may settle on the sample in static corrosion tests and inhibit corrosion processes. Furthermore, static corrosion tests permit the accumulation of soluble corrosion products in the acid that may also hinder the corrosion process. Therefore, a flowing sulfuric acid loop that provides a continuous, uncontaminated source of sulfuric acid will have to be constructed to assess the dynamic corrosion behavior of the alloys identified in this study if they are to be used in a sulfuric acid decomposition loop.

References

Brown, L.C., Besenbruch, G.E., Lentsch, R.D., Schultz, K.R., Funk, J.F., Pickard, P.S., Marshall, A.C., Showalter, S.K., "High Efficiency Generation of Hydrogen Fuels Using Nuclear Power", General Atomics Report, GA-A24285, June 2003.

Brown, L.C., Funk, J.F., Showalter, S.K., "High Efficiency Generation of Hydrogen Fuels Using Nuclear Power", General Atomics Report, GA-A23451, July 2000.

Kubo, S., Nakaiima, H., Kasahara, S., Higashi, S., Masaki, T., Abe, H. and Onuki, K., "A demonstration study on a closed-cycle hydrogen production by the thermochemical water-splitting iodine-sulfur process", Nuclear Engineering and Design, vol. 233, 2004, pp. 347-354.

Rodda, J.R., and Ives, M.B., "Determination of Corrosion Rates in Hot, Concentrated Sulfuric Acid", Corrosion, vol. 59, no. 4, 2003, pp. 363-370.

Trester, P.W. and Staley, H.G., "Assessment and Investigation of Containment Materials for the Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production: Final Report, July 1979 – December 1980", Gas Research Institute Report GRI-80/0081, 1981.

Wong, B., Brown, L.C., Buckingham, R., Besenbruch, G.E., Polansky, G. and Pickard, P., "Engineering Materials Requirements Assessment for the S-I Thermochemical Cycle", General Atomics Report GA-A24902, April 2005.